Rafaela Cunha de Barros da Silva Santos
Licenciada em Ciências da Engenharia Química e Bioquímica

Smart Windows with Permanent Memory Effect

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Orientador: Prof. Doutor João Carlos da Silva Barbosa Sotomayor

Júri:

Presidente: Prof. Doutora Maria Ascenção Carvalho Fernandes Miranda Reis
Arguente: Doutor Luis Ever Aguirre

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Departamento de Química

Smart Windows with Permanent Memory Effect

By

Rafaela Cunha de Barros da Silva Santos

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Smart Windows with Permanent Memory Effect

À minha avó Nini,
Esteja onde estiver, estará sempre comigo

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Abstract

In this work PDLC films were made with liquid crystal E7 marketed by MERCK®. Two monomers and one oligomer were used, the monomer PE4A (Pentaerythritol tetraacrylate), the monomer TMT (Trimethylolpropane trimethacrylate) and the oligomer AP [Poly(propylene glycol) acrylate]. The PDLC's were obtained by PIPS method and produced by thermal polymerization using a polymerization initiator AIBN.

A co-polymerization was studied using different proportions of PE4A and AP.

Electro-optical studies were made in order to determine the permanent memory effect of the PDLCs. Best results are for PE4A/AP co-polymerization of 50/50 and 60% of liquid crystal which results in obtained 100% of permanent memory effect.

Different techniques were carried out to characterize the PDLCs: Scanning Electron Microscopy in order to study the morphology of the polymer network, Polarized Light Microscopy which allowed to observe the distribution of the liquid crystal molecules in the polymer network before and after the application of an electric field and, with a temperature ramp at 1ºC/min, allows determine the clarification temperature of the PDLC, Differential Scanning Calorimetry to determine the T_g of monomers/oligomers and polymers, the nematic-isotropic temperature of the liquid crystal E7 and of the liquid crystal in the polymer network and viscosity measurements in order to understand if the viscosity can influence polymerization rate and the final matrix structure.

Scale-up was development in self-made cells using conductive glasses with polyimide alignment layer.

In order to erase the permanent memory effect obtained in the studied PDLCs, a device using Joule heating was tested.

Resumo

No decorrer deste trabalho foram feitos filmes de PDLC utilizando o cristal líquido E7 comercializado pela MERCK®. Foram utilizados dois monómeros e um oligómero, o monómero PE4A (Pentaerythritol tetraacrylate), o monómero TMT (Trimethylolpropane trimethacrylate) e o oligómero AP [Poly(propylene glycol) acrylate]. Os PDLC's foram obtidos através do método de separação de fases induzida por polimerização e polimerizados termicamente utilizando um iniciador de polimerização, AIBN.

Foi estudada uma co-polimerização utilizando-se diferentes proporções de PE4A e AP.

Fizeram-se estudos eletro-óticos de modo a determinar-se o efeito de memória permanente que os PDLCs apresentavam, com a co-polimerização usando uma proporção de PE4A/AP de 50/50 e uma percentagem de cristal líquido de 60% foi obtido 100% de efeito de memória permanente.

Realizaram-se diferentes técnicas para caracterizar os PDLCs: Microscopia Eletrónica de Varrimento com o objetivo de se estudar a morfologia da rede polimérica, Microscopia de Luz Polarizada que permitiu observar a distribuição do cristal líquido na rede polimérica antes e depois da aplicação de um campo elétrico e, aumentando a temperatura do PDLC a uma velocidade de 1ºC/minuto foi possível determinar a temperatura de clarificação do PDLC, Calorimetria Diferencial de Varrimento para determinar as T_g dos monómeros/oligómeros e dos polímeros, a temperatura nemática isotrópica do cristal líquido E7 e do cristal líquido na rede polimérica e foram realizadas medições de viscosidade com o objectivo de perceber se a viscosidade poderia influenciar a velocidade de polimerização e a estrutura final da matriz polimérica.

Fez-se o scale-up, com células produzidas no laboratório utilizando-se dois vidros condutores com uma camada de alinhamento de poliimida.

De forma a apagar o efeito de memória obtido nos PDLCs estudados utilizou-se uma fonte elétrica que aquece os PDLCs através de Efeito de Joule.

Table of Abbreviations

5CB	4-Cyano-4'-n-pentyl-1,1'-biphenyl
5CT	4-cyano-4''-n-pentyl-1,1',1''-terphenyl
7CB	4-cyano-4'-n-heptyl-1,1'-biphenyl
8OCB	4-cyano-4'-n-octyloxy-1,1'-biphenyl
A	Gradient velocity
AIBN	α,α-azobisisobutyronitrile
AP	Poly(propylene glycol) acrylate
c	Velocity of light in vacuum
DSC	Differential Scanning Calorometry
E	Electric field
E7	Nematic liquid crystal
$\mathbf{E_{90}}$	Electric field required to achieve 90% of the maximum transmittance
EO	Electro-Optical
f	Shearing stress
ITO	Indium tin oxide
LC	Liquid crystal
n	Director of the liquid crystal
$\mathbf{n_0}$	Ordinary index
$\mathbf{n_e}$	Extraordinary index
$\mathbf{n_{iso}}$	Refractive index of isotropic liquid
$\mathbf{n_p}$	Refractive index of the polymeric matrix
PDLC	Polymer dispersed liquid crystal
PE4A	Pentaerythritol tetraacrylate
PIPS	Polymerization induced phase separation
POM	Polarized Optical Microscopy
$\mathbf{S_A}$	Smectic phase A
$\mathbf{S_C}$	Smectic phase C
SEM	Scanning Electron Microscope
SIPS	Solvent induced phase separation
$\mathbf{T_0}$	Initial transmittance (%)
$\mathbf{T_c}$	Clarification temperature
$\mathbf{T_f}$	Melting point
$\mathbf{T_G}$	Glass transition temperature
TIPS	Thermally induced phase separation
$\mathbf{T_{Máx}}$	Maximum transmittance when the voltage is applied (%)
TMT	Trimethylolpropane trimethacrylate
$\mathbf{T_{NI}}$	Nematic-isotropic transition temperature
$\mathbf{T_{off}}$	Transmittance when the voltage is removed (%)
Δn	Value of birefringence
η	Viscosity
μ	Magnetic permeability of the material

$\varepsilon_{\parallel}$	parallel dielectric constant
$\varepsilon\perp$	perpendicular dielectric constant
v	Velocity of light in material
Δε	Dielectric anisotropry
(%)C	Percentage of contrast of the memory state
(%)PME	Percentage of permanent memory effect

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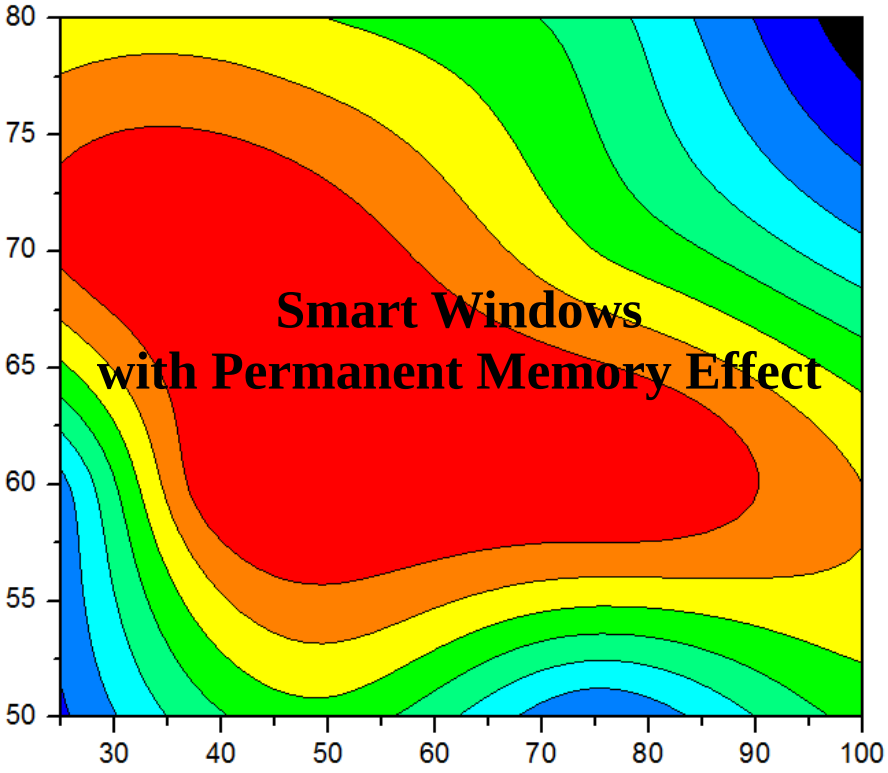
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I. Chapter One

1. Introduction

1.1. Liquid Crystals

Liquid crystals are seen as fourth state of matter. They are an intermediate state between the liquid phase and the solid phase, a transition phase occurring between T_f and T_c, T_f is the melting point and T_c the clearing point.

The difference between liquid and the liquid crystal phases is related to the ordering of molecules. In liquid crystal phase molecules have a certain orientation, they have lost positional order but still have orientational order, and in an isotropic liquid state molecules are totally disoriented. [1]

Figure II.1 shows the orientational difference between the different phases.

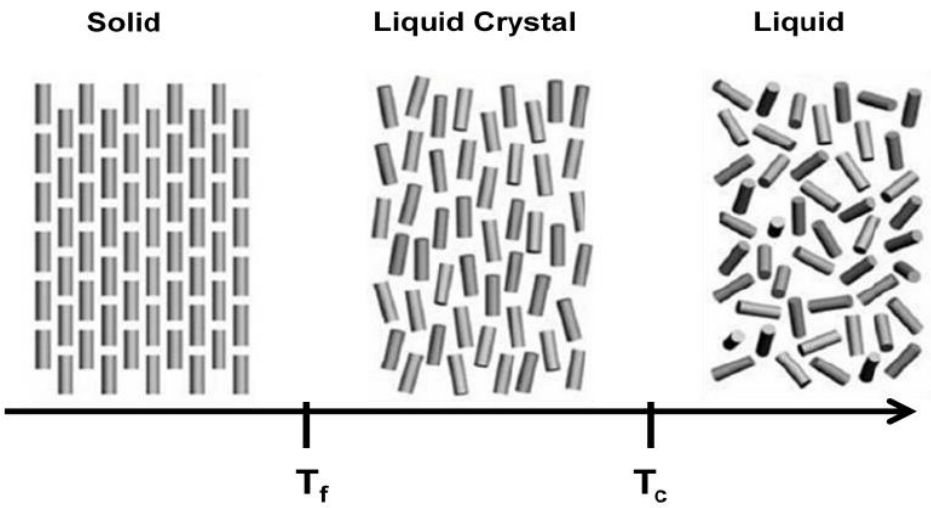


Figure I.1 - Schematic illustration of a solid, liquid crystal and liquid phases [2] **adapted**

1.1.1. Properties of Liquid Crystals

The main properties of the liquid crystals are the fact that the liquid crystals are anisotropic. The anisotropy distinguishes liquid crystals from isotropic liquids. Liquid crystals have these properties because they have a small degree of order among the molecules. [3]

This anisotropy manifests itself in the elastic, electric, magnetic and optical properties of a material. [3]

Anisotropy implies that all the measurements of an elastic modulus, dielectric constant, magnetic susceptibility, or refractive index give different results depending on the direction along which it is measured. [3]

Figure I.2 show a schematic illustration to explain anisotropy, the image that is observed depends on the direction that is observed.

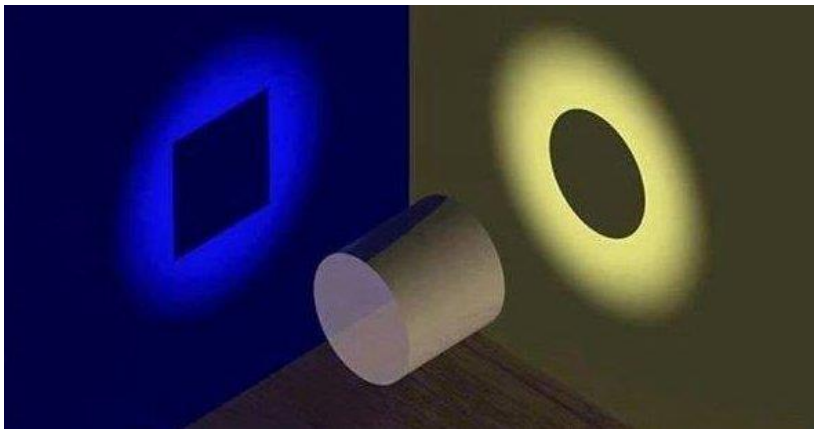


Figure I.2 – Schematic illustration

Liquid crystals shows two types of anisotropy, optic and dielectric. Optic anisotropy is related to the refractive indices, the ordinary index (n_0) and the extraordinary index (n_e). The dielectric anisotropy defines the orientation of the liquid crystal in the presence of an electric field, characterized by two dielectric constants: parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) to the principal axes of the molecule. [4]

The extraordinary index (n_e) and the ordinary index (n_0) are measured with two different ways. The extraordinary index (n_e) is measured for the light wave where the electric vector vibrates along the optical axis and the ordinary index (n_0) is measured for the light wave where the electric vector vibrates perpendicular of the optical axis. [2]

Figure I.3 show the light propagation in liquid crystals.

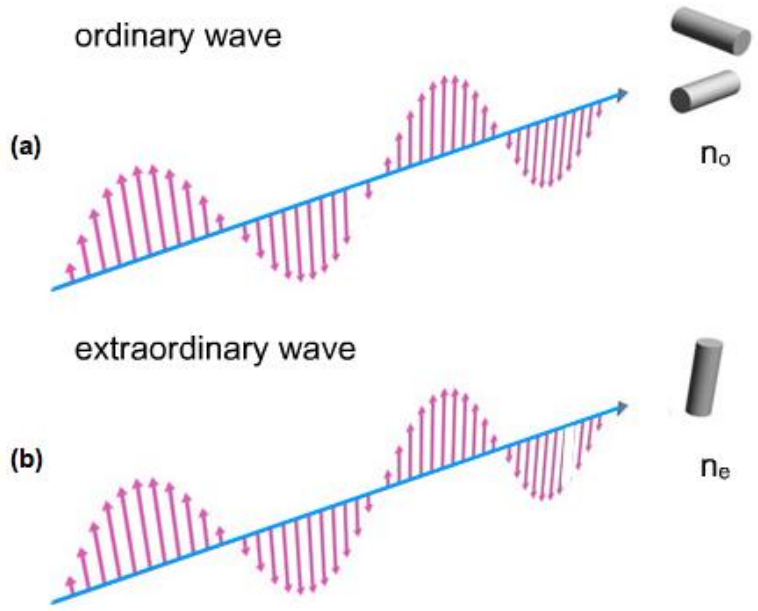


Figure I.3 - Light propagation in Liquid Crystals along and normal to optical axis: (a) ordinary beam (b) extraordinary beam
n_e- extraordinary refractive index; n_0- ordinary refractive index [2]

An important property of liquid crystals is the birefringence

The refractive index is defined by the next equation:

$$n_e = \frac{c}{v_e} \quad \text{and} \quad n_0 = \frac{c}{v_0}$$

Where:

c: Velocity of light in vacuum;

v: Velocity of light in material

The value of birefringence of a material it is given by the difference between the two refractive indices, Δn. [2]

$$\Delta n = n_e - n_0$$

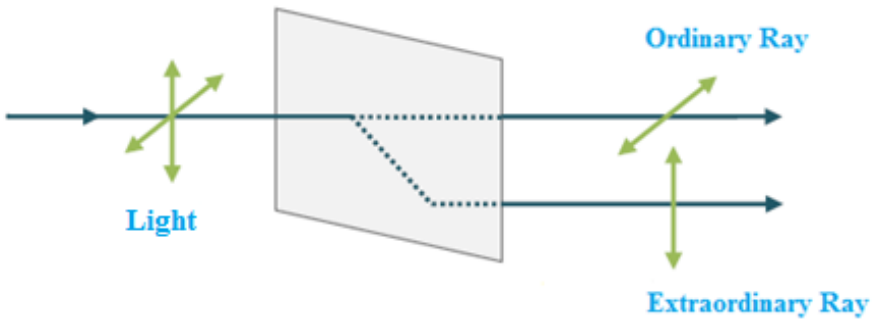


Figure I.4 - Light travelling through a birefringent material [5] (adapted)

The birefringence of liquid crystals decreases with the increases of temperature. [2]

Figure I.5 show the temperature dependence of refractive indices.

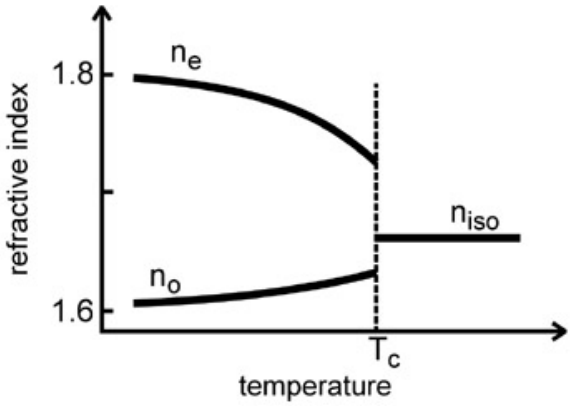


Figure I.5 - Temperature dependence of refractive indices
T_C: Clearing temperature; n_{iso}: Refractive index of isotropic liquid [2]

1.1.2. Types of liquid crystal

Liquid crystal phases can be divided in two groups: thermotropics and lyotropics.

The thermotropic liquid crystalline materials do not require a solvent to form liquid crystalline materials. [6]

In thermotropic phase it is possible to differentiate two types: calamitic and discotic.

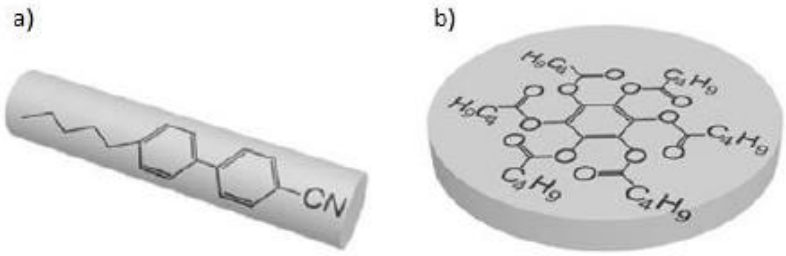


Figure I.6 - Thermotropic liquid crystal molecule [2]

Figure I.6 a) show the molecular structure of 4-cyano-4'-n-pentyl-1,1'-biphenyl, showing a calamitic structure. Figure I.6 b) show the molecular structure of benzene-hexa-n-pentanoate, showing a discotic structure. [2]

The lyotropic liquid crystalline phase requires a presence of a solvent to form liquid crystalline material. [6]

Figure I.7 - Lyotropic liquid crystal molecule [2]

Figure I.7 show the molecular structure of sodium dodecyl sulfate, this kind of molecules have a hydrophilic polar head and a hydrophobic non-polar tail. [2]

The liquid crystal used in the present work, E7 by Merck, is a thermotropic calamitic liquid crystal and will be described in chapter 2.

✓ Thermotropic Phases of a liquid crystal

There are three different phases of thermotropic calamitic liquid crystals: nematic, cholesteric and smectic phases.

- Nematic phase

In this phase the molecules have no positional order, but they have orientational order. The molecules orient themselves parallel to one another. [1]
Figure I.8 show the structure of a Nematic liquid crystal.

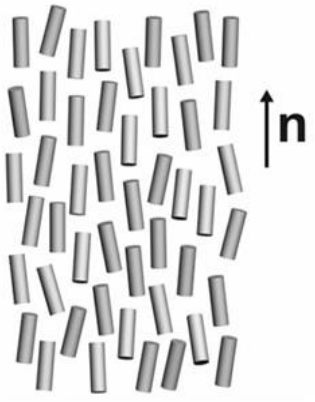


Figure I.8 - Structure of a nematic liquid crystal phase [2]

In the nematic phase the molecules have a preferential orientation and this orientation can be represented for an unitary vector, n, the direction vector. [2]

- Cholesteric phase

The cholesteric consist of a quasi-nematic layers, whose individual directors are turned by a fixed angle on proceeding from one layer to the next. [2]

Figure I.9 show the structure of cholesteric liquid crystals.

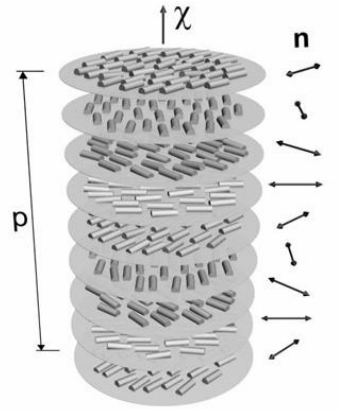


Figure I.9 - Structure of cholesteric liquid crystals [2]

In each layer the molecules have an orientational order, this order varies according to a helical conformation.

- Smectic phase

In this phase the molecules organize themselves in overlapping layers. There are two different smectic phases: smectic phase A (S_A), when the direction vector are perpendicular to the surface of the layer and the smectic phase C (S_C) when the direction vector form an angle different to zero with the normal to the surface. [7]

Figure I.10 and Figure I.11 show the structure of smectic phase A (S_A) and smectic phase C (S_C).

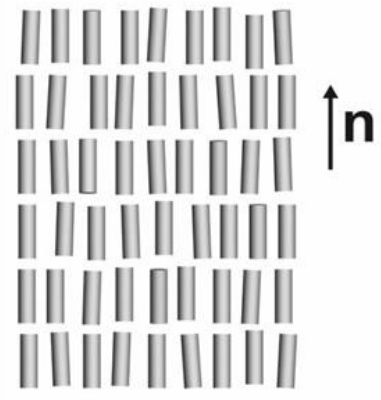


Figure I.10 - Structure of smectic A (S_A) liquid crystal [2]

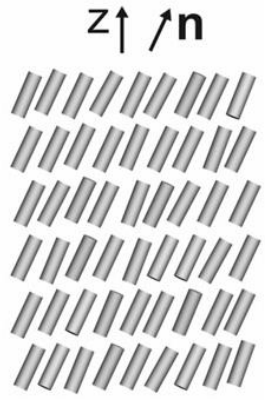


Figure I.11 - Structure of smectic C (S_C) liquid crystal [2]

In each mesophase, S_A and S_C, the molecules in each layer have a positional order. [7]

1.1.3. Liquid Crystals in an electric field

When an electric field is applied in a nematic liquid crystal it is possible that such application can move positive and negative charges in different directions, so, a dipole is produce, only when an electric field it is applied, this dipole is named induced dipole. [6]

If the dipole moment is parallel to the molecular axis, then $\Delta\varepsilon > 0$ and the molecules tend to orient along the electric field direction. [2]

Figure I.12 show the behavior of the molecules of LC, with $\Delta\varepsilon > 0$, in the absence (off) and presence (on) of an electric field.

Figure I.12 - Effects of an electric field in a liquid crystal molecule [5]

1.2. Polymer Dispersed Liquid Crystal

Polymer Dispersed liquid Crystal (PDLC) is a film constituted by micro domains of liquid crystal dispersed in a polymeric matrix. [7]

There are several ways to prepare a PDLC: by emulsion and phase separation. In the first case, emulsion, the system remains heterogeneous during the process and in the second case, phase separation, the system becomes heterogeneous. [8]

In the phase separation there are three different ways to prepare a PDLC: TIPS (Thermally Induced Phase Separation), SIPS (Solvent Induced Phase Separation) and PIPS (Polymerization Induced Phase Separation). [9]

In this work the PIPS method was performed by thermal polymerization of a homogeneous mixture of polymerizable monomers/oligomers, liquid crystal and an initiator.

The PIPS method consists in mixing the liquid crystal with a monomers/oligomers, which act as a solvent for the liquid crystal. Polymerization can be induced through the application of heat. The growing polymer chains phase separates from the liquid crystal to form a matrix. [10]

The main advantage of preparation by PIPS method is the possibility to obtain a composite directly between glass plates coated with conductive indium tin oxide film without additional laminating procedures. [8]

PDLC devices can be switched from an opaque scattering state to a transparent state when an electric field is applied. The polymer matrix material is optically isotropic so it has a single refractive index (n_p). The liquid crystal within the micro-domains has an ordinary refractive index (n_0) and an extraordinary refractive index (n_e). When an electric field, with sufficient strength to overcome the interactions between polymer matrix and liquid crystal at interfaces of LC domains in the polymer matrix, is applied across the film liquid crystal directors within each droplet become uniformly oriented parallel to the direction of the field. [8]

If the refractive index of the LC matches with the refractive index of the polymeric matrix the film becomes transparent. [8]

Figure I.13 show a schematic illustration of the average molecular orientation of the liquid crystal within micro droplets without and with an applied field.

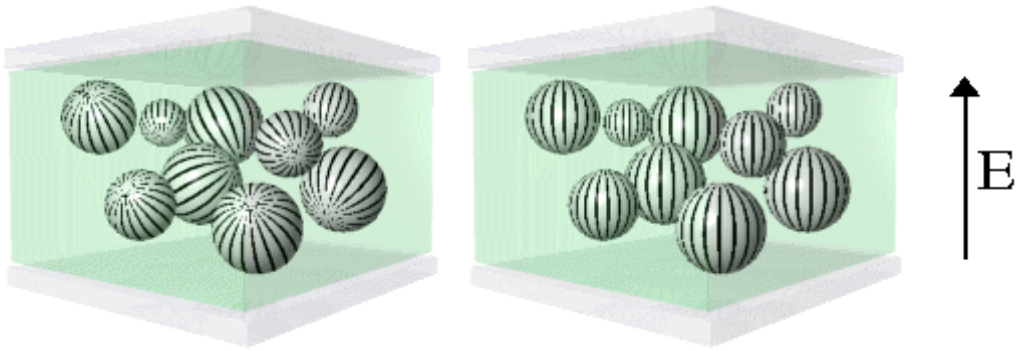


Figure I.13 - Schematic representation of the average molecular orientation of the liquid crystal within the micro droplets without and with an applied field [11] adapted

It is possible to observe through the Figure I.14 that with the increase of the number of polymerizable groups, the polymer network becomes more crosslinked. [12]

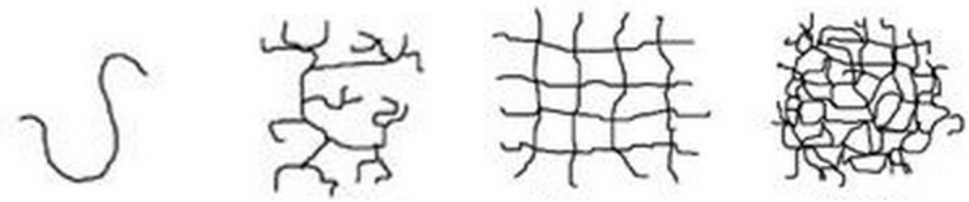


Figure I.14 - Evolution of the polymer network with the increasing of the number of the polymerizable groups of the monomer [13]

In this work a monomer with three polymerizable groups (TMT), one monomer with four polymerizable groups (PE4A) and a co-polymerization with a monomer with four polymerizable groups (PE4A) and an oligomers with one polymerizable group (AP) were studied.

This three different monomers/oligomers were studied in order to increase the crosslinked of the polymer network and determinate if the permanent memory effect is influenced by this variation.

1.2.1. Polymer Dispersed Liquid Crystal Matrix Morphology

The polymerization conditions, the nature of the liquid crystal and the polymerizable monomers determine the morphology of the polymer matrix.

There are two different morphologies in the PDLC: "Swiss Cheese" morphology and "Polymer Ball" morphology.

✓ *"Swiss Cheese" Morphology*

In this morphology, liquid crystal droplets are embedded in the polymer matrix. [4] The characteristics of this morphology and of the LC micro droplets are in strong dependence on the parameters of the preparation and the type of polymeric matrix. [8]

Figure I.15 show a SEM image for Swiss Cheese morphology.

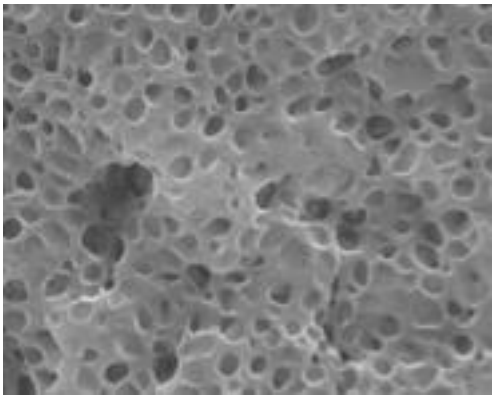


Figure I.15 - SEM image for Swiss Cheese morphology [14]

The liquid crystal molecules can have three different types of alignment with the polymer: Radial, Bipolar and Axial configuration.

The radial configuration occurs when the liquid crystal molecules are anchored with their long axes perpendicular to the droplet walls. [11]

Figure I.16 show the liquid crystal droplets with radial configuration.

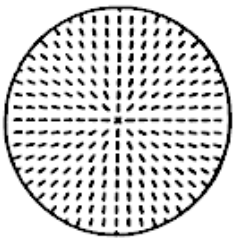


Figure I.16 - Radial configuration of a LC droplet [11]

The axial configuration of the liquid crystal droplets also occurs when the molecules are oriented perpendicular to the droplet wall, but only when there is weak surface anchoring. [11]

Figure I.17 show the liquid crystal droplets with axial configuration.

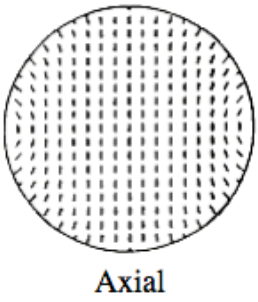


Figure I.17 - Axial configuration of a LC droplet [11]

The bipolar configuration is obtained by tangential anchoring of the liquid crystal molecules, this creates two points defects at the poles of the droplet. [11]

Figure I.18 show the liquid crystal droplets with bipolar configuration.

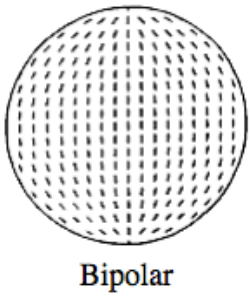


Figure I.18 - Bipolar configuration of a LC droplet [11]

✓ *"Polymer Ball" Morphology*

In Polymer ball morphology the polymerizable monomers are phase-separated from the continuous liquid crystal and forms micro sized polymer balls, these micro sized polymer balls merge and form a large polymer network structure with diverse shapes of voids in which liquid crystal exists. [14]

The polymer ball morphology it is characterized by asymmetric voids in the polymer matrix in which the liquid crystal exists. [10]

Figure I.19 show a SEM image for Polymer Ball morphology.

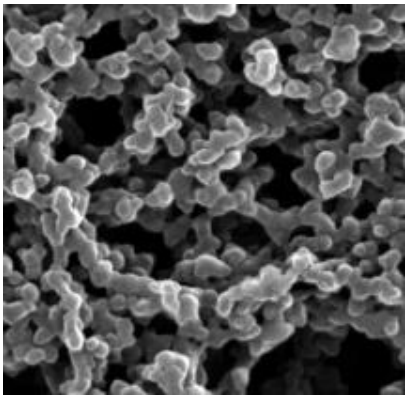


Figure I.19 - SEM image for Polymer Ball morphology [8]

1.2.2. Permanent memory effect and hysteresis

As described above, the PDLC can be switched from the opaque to the transparent state through the application of an electric field. When an electric field is applied it is possible to observe different types of electro-optical response, with hysteresis and without hysteresis.

The electro-optical response of PDLC is usually measured by ramping a PDLC up and down in voltage and comparing the optical response at each voltage. [10]

One of electro-optical response for PDLC is when the increasing voltage curves is coincident to the decreasing voltage curve, electro-optical response without hysteresis When these curves are not coincident the PDLC show electrical hysteresis, this happens when transmittance with increasing voltage is lower than the transmittance when the electric field is decreased. [8]

Figure I.20 show an electro-optical response without (A) an with (B) hysteresis.

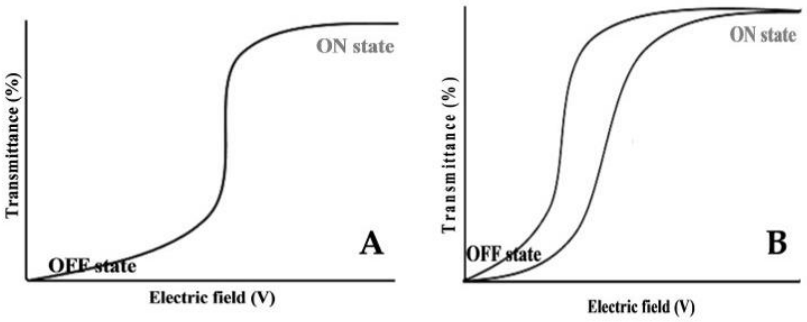


Figure I.20 - Electro-optical response of PDLC
A: Without hysteresis; B: With hysteresis [8]

When the electric field is removed, in some PDLC films, it is possible to observe that the transmittance do not return to the initial value, this effect is called permanent memory effect (PME). This permanent memory effect occurs since the liquid crystal molecules could not relax back completely, but the molecules remain aligned in the direction of the electric field after its removal. [15]

Figure I.21 show an electro-optical response with permanent memory effect.

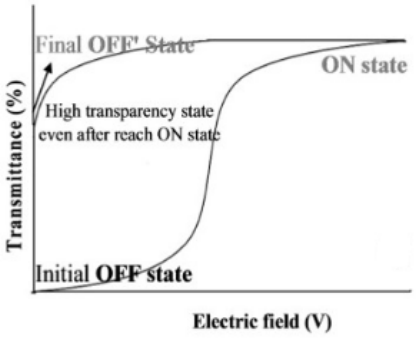


Figure I.21 - Electro-optical response of PDLC with permanent memory effect [8]

In Figure I.1Figure I.21 the initial OFF state corresponds to the transmittance of the initial state, opaque state, where the applied electric field is zero.

It is possible to quantify several factors to characterize the permanent memory effect: the permanent memory effect (%PME), E90 and %C.

The permanent memory effect is defined by:

$$(\%)PME = \frac{T_{off} - T_0}{T_{Máx} - T_0} \times 100$$

T_0 - Initial transmittance (%)
$T_{Máx}$ – Maximum transmittance when the voltage is applied (%)
T_{off} – Transmittance when the voltage is removed (%)

The percentage of memory state contrast can be defined by:

$$(\%)C = T_{off} - T_0$$

The E_{90} is the electric field required to achieve 90% of the maximum transmittance.

The permanent memory effect is thermally destroyed at a certain clarification temperature that is, normally, below the nematic isotropic temperature. [14]

1.2.3. Surface anchorage

The orientation of liquid crystal molecules is affected by the interaction between the polymeric matrix and the domains of liquid crystal, this interaction as called anchorage. [16]
In nematic liquid crystals there is a relationship between the size and the shape of the liquid crystal domains and the anchoring effect. [8] When the shape and the size of liquid crystal domains increases the anchoring effect decrease. Strong anchoring forces hinder the alignment of liquid crystal molecules when an electric field is applied, which implies that the permanent memory effect decreases with the increase of anchoring effect. [19]
Figure I.22 and Figure I.23 show an example of the alignment of liquid crystal molecules in the polymeric matrix without and with an electric field.

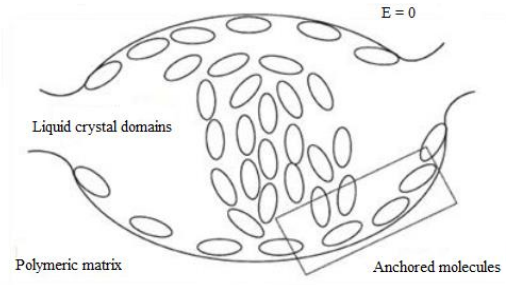


Figure I.22 - Example of anchoring of liquid crystal molecules in the polymeric matrix with E = 0 [12]

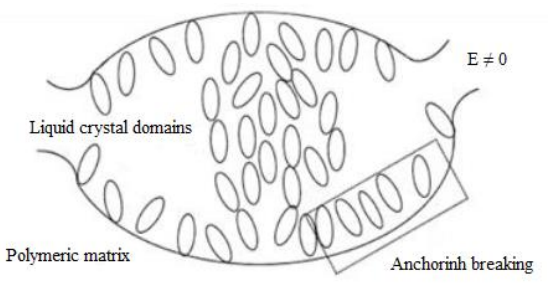


Figure I.23 - Example of anchoring of liquid crystal molecules in the polymeric matrix with E ≠ 0 [12]

1.2.4. PDLC applications

Due to its ability to switch from an opaque state to a transparent state, when an electric field is applied, PDLC have a variety of applications as reflective displays, electrically light shutters and holographic gratings. [14] [17]

The most popular application for PDLC are the smart windows. Smart windows are composed by two conductive glasses, between theses glasses is placed a PDLC. Initially the window is opaque, but with the application of an electric field the window switch to a transparent state.

The PDLC with permanent memory effect only needs heat to switch to a transparent state, when the PDLC is transparent remains transparent until heat is applied, when this happen the PDLC returns to the opaque state.

Figure I.24 show an example of a smart window in on state (transparent) and off state (opaque).

Figure I.24 - Example of a smart window [18]

Another property of PDLC with permanent memory effect is the possibility to store optical information in PDLC film. Is possible to write information with applied voltage, read the written information in a digital way (opaque or transparent states) and erase the information with the increase of temperature. After erase the information the devise returns to the opaque state. [19]

Figure I.25 show a representative scheme of digital writing.

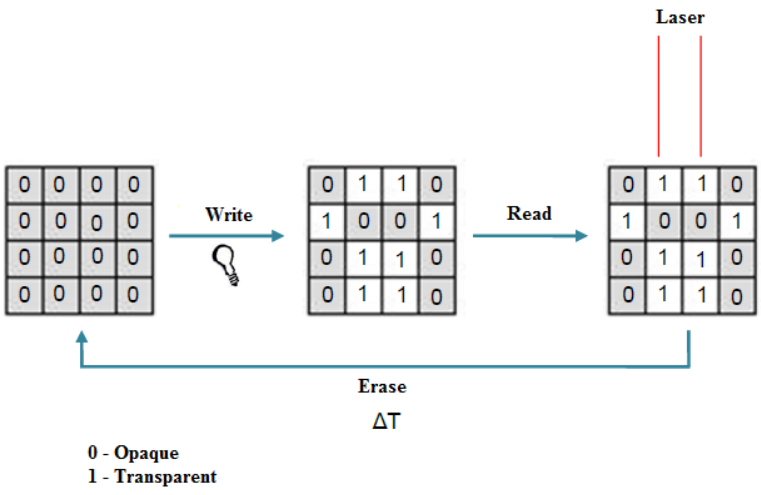


Figure I.25 - Representative scheme of digital writing [5] adapted

II. Chapter Two

2. Materials and Methods

2.1. Materials

2.1.1. Monomers and oligomers

In this work, three commercial oligomers/monomers were used.

- ✓ Trimethylolpropane trimethacrylate (TMT)

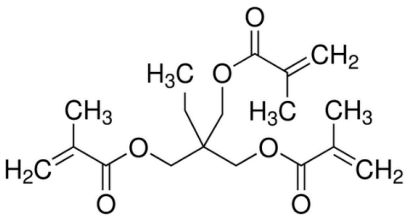


Figure II.1 - Molecular structure of TMT [20]

The monomer TMT has a molecular weigth of 338.40 g/mol and CAS number is 3290-92-4. [20]

- ✓ Poly(propylene glycol) acrylate (AP)

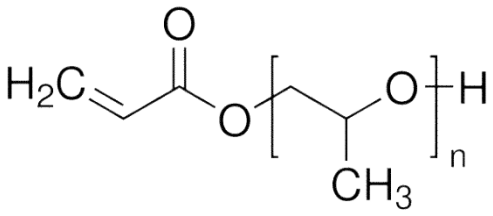


Figure II.2 - Molecular structure of AP [21]

The oligomer has a average molecular weigth of, approxymately, 475 g/mol and CAS number is 50858-51-0. [21]

✓ Pentaerythritol tetraacrylate (PE4A)

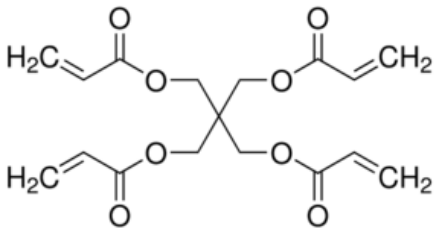


Figure II.3 - Molecular structure of PE4A [22]

The monomer PE4A has a molecular weight of 352.34 g/mol and CAS number is 4986-89-4. [22]

2.1.2. Liquid Crystal

The liquid crystal used in this work is E7, commercially by Merkc®. This liquid crystal is a blend of various compounds forming a nematic liquid crystal.

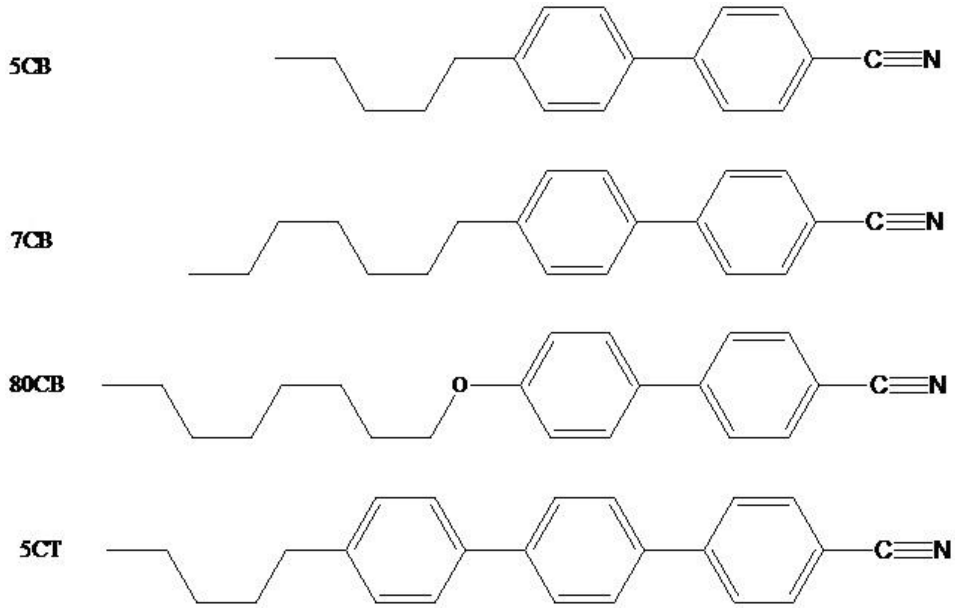


Figure II.4 - Chemical structure of the components of E7 [8]

Figure II.4 show the chemical structures of E7 components and the Table II.1 show the designation of each component and the respective component percentage in the mixture, calculate by high pressure liquid chromatography.

Table II.1 - Composition of E7 [8]

Designation	Molecular structure	IUPAC name	Composition in the mixture	T_{NI} (ºC)
5CB	$C_{18}H_{19}N$	4-Cyano-4'-n-pentyl-1,1'-biphenyl	51%	35.3
7CB	$C_{20}H_{23}N$	4-cyano-4'-n-heptyl-1,1'-biphenyl	25%	42.8
8OCB	$C_{21}H_{25}NO$	4-cyano-4'-n-octyloxy-1,1'-biphenyl	16%	80
5CT	$C_{24}H_{23}N$	4-cyano-4''-n-pentyl-1,1',1''-terphenyl	8%	240

This liquid crystal show a single nematic to isotropic transition (T_{NI}) at 58.3ºC and a glass transition (T_G) at -62ºC. [23] [24]

2.1.2. Initiators

The polymerization starts using agents able to form free radicals, which are denominated polymerization initiators. These initiators are decomposed using energy, in form of light or heat. In this work one thermal initiator, α,α-azobisisobutyronitrile were used.

- ✓ α,α-azobisisobutyronitrile

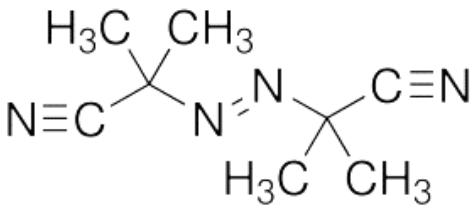


Figure II.5 - Molecular structure of AIBN [21]

The molecular weight of AIBN is 164.21 g/mol and CAS number is 78-67-1. [21]

The formation of free radicals starts at 64ºC.

Figure II.6 show the formation of free radicals.

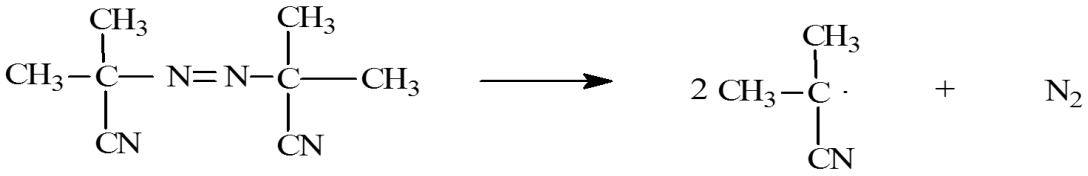


Figure II.6 - Decomposition of AIBN [8]

Each mixture has 1% of polymerization initiator (AIBN), elated to monomer/oligomer weight.

2.1.3. Commercial Cells and Conductive Glasses

The cells for electro-optic studies were made by conducting glass coated by a layer of indium tin oxide (ITO).

Figure II.7 show a schematic ilustration of an ITO cell, LC2-20 by Instec [25]

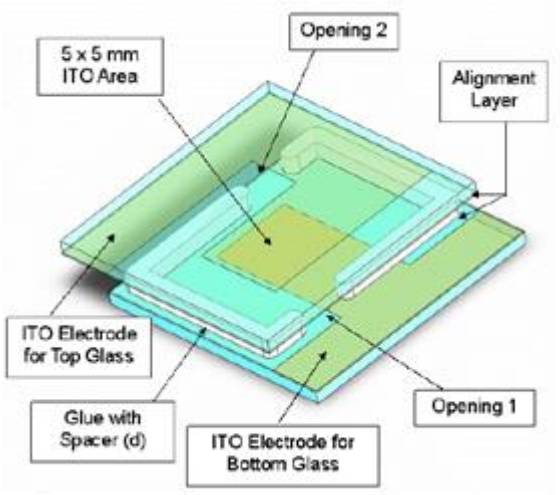


Figure II.7 - Schematic illustration of an ITO cell [25]

Cell spacing is 20 µm and cell thickness is 1.5 mm and the ITO area occupies 25 mm^2 of the cell and this is the only area where voltage is applied where a resistance up to 100 Ω/□.[25]

To make the scale-up two conductive glasses with an area of 5 cm^2 were used, these glasses has a polyimide alignment layer.

Figure II.8 show a schematic illustration for the glasses used to make the self-made cells in this work.

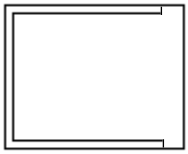


Figure II.8 - Schematic illustration of a glass to make a self-made cell

The self-made cells are constructed using two conductive glasses with a polyimide alignment layer, the spacing between the two glasses is achieve using a mylar with 23 µm of thickness.
In the self-made cells the conducive area it is around 3 cm^2.
In Figure II.9 is possible to observe a schematic illustration for the self-made cell.

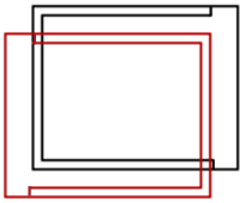


Figure II.9 - Schematic illustration for a self-made cell

The main difference between the commercial cells and the self-made cells is the conductive area and the type off spacers.

The commercial cells and the glasses are commercialized by Instec.

2.2. Methods

2.2.1. Preparation of solutions

The solutions used in this study are a homogeneous mixture of monomer/oligomer, liquid crystal and an initiator in different proportions. In this work a co-polymerization between one monomer and one oligomer (PE4A and AP), the monomer TMT and the monomer PE4A were studied. Each solution has 0.5g. The initiator correspond a 1% (w/w) of the monomer weight.
All solutions were weighted on a scale RADWAG analytical balance with four decimal digits.

All monomers/oligomers are commercialized with an inhibitor of polymerization. In order to remove the inhibitor of polymerization the monomers/oligomers were passed through a column filled with a resin, polystyrene divinylbenzene, and is commercialized by Merck®.
The mixture needs to be homogenized before placing in the ITO cells. There are used a vortex to homogenize the solutions.

2.2.2. Preparation of PDLC

In this work the preparation of the PDLC was made by phase separation by PIPS. This method consists in the preparation of a homogeneous mixture, compost by the monomer/oligomer, liquid crystal and an initiator. The polymerization starts at 64ºC, at this temperature the initiator forms the free radicals.

After the start of polymerization the liquid crystal begins to cluster into micro domains that arises in the polymeric matrix.

2.2.3. Polarized Light Microscopy analysis

A polarized optical microscope is a microscope that uses polarized light for investigating the optical properties of species, is frequently used to study the morphology of the anisotropic materials.

The microscope used in this work are the Olympus BH-2 optical polarizing microscope equipped with a Mettler Toled FP82HT hot stage (20ºC to 200ºC). The microstructures of the sample was monitored by taking microphotographs at determinate temperatures, using an Olympus Caedia C-5060 digital camera interfaced to a computer.

Figure II.10 show the microscope used in this work.

Figure II.10 - Microscope whit crossed polarizers

The polarized light microscope have two polarizers, one placed in the path of the beam before it reaches the material and a pipe between the objective and the eyepiece. The resulting contrast observed in the image arises from the interaction of polarized light with a birefringent sample plan, thus producing two perpendicular components: the extraordinary ray and the ordinary ray. [26]

Figure II.11 explained the fundamental of cross polar microscope.

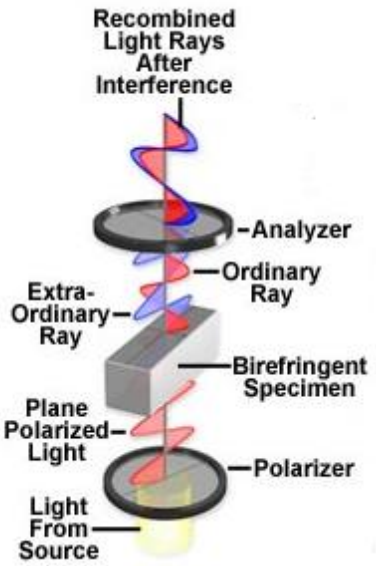


Figure II.11 - Functional diagram of POM [26]

2.2.4. Scanning Electron Microscopy analysis

SEM analysis is a technique of microscopy that use an electron beam to analyze the samples in a fine scale.

SEM analysis, gives the possibility to study the structure of the polymeric matrix and gives the possibility to available the spaces occupied by the liquid crystal.

The SEM used in this work is placed at CENIMAT FCT-UNL, SEM images were acquired by a Carl Zeiss Auriga crossbeam and the instrument were equipped with an Oxford energy dispersive X-Ray spectrometer. [27]

Figure II.12 show the SEM installations on CENIMAT.

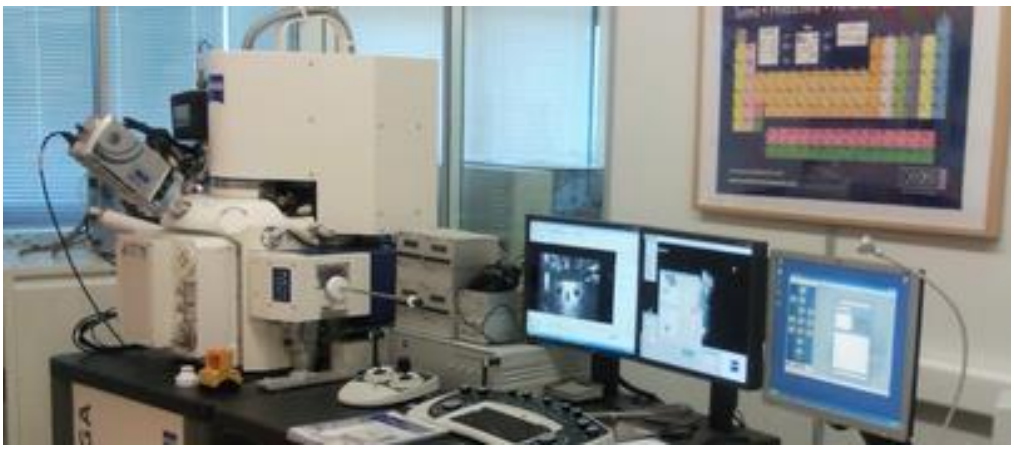


Figure II.12 - SEM at Cenimat, FCT-UNL [27]

- ✓ Sample preparation

Samples were polymerized in a Teflon disc at 74ºC. After the polymerization the liquid crystal was removed by acetonitrile. The samples were dried for a few days in a desiccator.
The sample was placed on a conductive metal support.

2.2.5. Electro-Optical analysis

The EO study of a PDLC allows the determination of several parameters from the measured transmittance. These parameters are: the maximum and the minimum transmittance, the E_{90}, the PME and the percentage of the memory state contrast.
The E_{90} is the voltage required to obtain 90% of the maximum transmittance. [6]
The transmittance is determined by the ratio between the intensity of the beam after passing through the sample and the initial intensity.
The experimental assembly consists in an optical part and in an electric part.
The optical part consists in a diode array Avantes Spectrophotometer, AvaLight-DHS and AvaSpec 2048, using a wavelength at 633 nm.
The electric pulse is generated by a programmable waveform generator, Wavetek 20 MHz Synthesized Functional Generator Model 90, which creates an AC wave with a low amplitude between 0V and 27V. The generator is linked to a Vtrek TP-430 amplifier reaching a voltage of 47V and a transformer that works in a reverse mode and extends the input voltage by a ratio of $\frac{220}{9}$. The amplifier is fed by a Kiotto KPS 1310 power supply and the output detector, AvaSpec-2048, is connected to a computer data acquisition software.
The voltage is measured using a multimeter, Iso-Tech IDM71, and the waveshape is observed by an oscilloscope, Tektronix TDS 210.
In the electric assembly there are two different resistances, the first resistance (1Ω) has the purpose of securing the amplifier of short-circuits and the second (150 kΩ) has the purpose to standardize the voltage wave.
Figure II.13 show the electro-optical assembly used in this work.

Figure II.13 - Electro-Optical assembly

Where,

1 – Housing lamps;

2 – Generator;

3 – Amplifier power supply;

4 – Transformer and resistances;

5 – Sample holder;

6 – Multimeter,

7 – Computer with analysis program;

8 – Amplifier;

9 – Oscilloscope.

The electro-optical study is divided in three different cycles, each cycle corresponding to $^{1}/_{3}$, $^{2}/_{3}$ and $^{3}/_{3}$ of the maximum voltage applied, this voltage correspond to, approximately, 400 V. Each cycle have 35 points with the voltage increasing and 35 points with the voltage decreasing and each point have the duration of 1.2 second.

In the pulse, the voltage is applied to the sample for 200 ms and for 1000 ms the voltage is not apply, five measures are performed: three during the first 200 ms and two over the next 1000 ms.

Figure II.14 show the electric pulse applied to the sample.

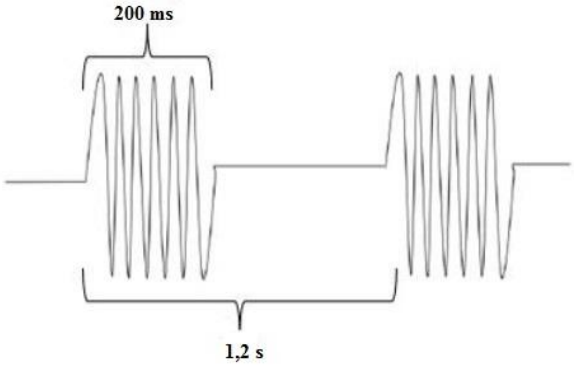


Figure II.14 - Electric pulse applied to the sample [12] adapted

All measurements were performed at 1 kHz.

2.2.6. Differential Scanning Calorimetry analysis (DSC)

Differencial Scnanning Calorometry is a thermal analysis technique that looks at how a material's heat capacity is changed by temperature. A sample of known mass is heated or cooled at a known velocity and the changes in the heatcapacity are tracked as changes in the heat flow. This allows the detection of transitions like melting, glass transitions and phase changes. [28]
The glass transition (T_g) is the temperature above which the translational movement of the molecules starts. At this temperature a state change occurs, from a glassy state to a "plastic" state. Below this temperature the molecules only have vibrational motion and the translational motion is "frozen". [29]

Figure II.15 show a schematic representation of the different transitions that can be observed in a DSC analysis.

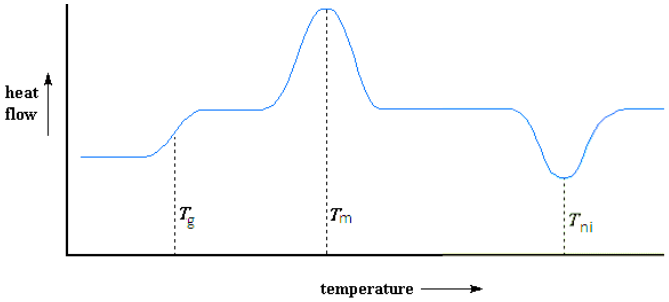


Figure II.15 - Variation of heat flow with temperature [30] adapted

Figure II.16 show the DSC equipment using in this work.

Figure II.16 - DSC equipment

2.2.7. Viscosity measurements

Viscosity is the quantity that describes a fluid's resistance to flow. Fluids resist the relative motion of immersed objects through them as well as to the motion of layers with differing velocities within them.

The viscosity is the ratio between the shearing stress and the velocity gradient: [31]

$$\eta = \frac{f}{A} \times \frac{dZ}{dv_x}$$

In this work the equipment used was a Bohlin Gemini Hr Nano Rotational Rheometer with a coni-plate geometry, at stationary method.

Figure II.17 show the equipment used in this work.

Figure II.17 - Viscosity measure equipment

2.2.8. Device to Erase the Permanent Memory Effect by Joule Heating

After the application of an electric field, the cell with PME lies transparent. To turn back opaque state, is necessary to heat the cell.

When there is an electric current in a conductor, the free electrons gain kinetic energy due to the work done on the free electrons by the field. However, steady state is soon achieved as the kinetic energy gain is continuously dissipated into the thermal energy of conductor by interactions between the free electrons and the lattice ions of the conductor, this mechanism for increasing the thermal energy of conductor is called Joule heating. [32]

The Joule heating produces heat, so, when the cell is subject to an electric current with a provide voltage the ITO layer is heated and the molecules of LC lose their orientation, so the PDLC returns to the initial opaque state.

The Joule heating is related with the current intensity and resistance of the material:

$$Q \propto I^2 R$$

Where,

Q is the Joule heating,

I is the intensity of the current,

R is the resistance

The Joule heating was used to erase the permanent memory effect.

The power supply used in this work is an AIM-TTi EX4210R, with a maximum voltage of 42V and a maximum current of 10A.

Figure II.18 show the power supply used in this work to produce Joule heating.

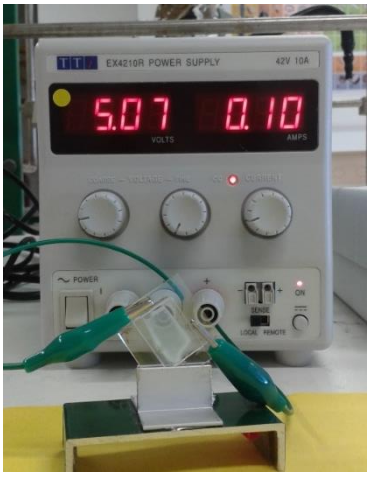


Figure II.18 – Power Supply used to produce Joule heating

III. Chapter Three

3. Experimental Results and Analysis

In this chapter, it will be described and analyzed the experimental results obtained in this work.
The performance of PDLCs films using the monomers TMT and PE4A and using a co-polymerization between the monomer PE4A and the oligomer AP were studied using different techniques: electro-optical studies in order to determine the permanent memory effect of the PDLCs, Scanning Electron Microscopy in order to study the morphology of the polymer network, Polarized Light Microscopy which allowed to observe the distribution of the liquid crystal molecules in the polymer network before and after the application of an electric field and, with a temperature ramp at 1ºC/min, allows determine the clarification temperature of the PDLC, Differential Scanning Calorimetry to determine the T_g of monomers/oligomers and polymers, the nematic-isotropic temperature of the liquid crystal E7 and of the liquid crystal in the polymer network and viscosity measurements in order to understand if the viscosity can influence polymerization rate and the final matrix structure.
Scale-up was development in self-made cells using conductive glasses with polyimide alignment layer.
In order to erase the permanent memory effect obtained in the studied PDLCs, a device using Joule heating was tested.

.

3.1. Study of the PDLC made by TMT polymer and E7 liquid crystal

The TMT is a monomer with three polymerizable groups, it was chosen a tri-methacrylate because wanted to study the crosslinked of the polymer network with the increase of the polymerizable groups.

3.1.1. Electro-Optical response

Figure III.1, Figure III.2, Figure III.3 and Figure III.4 show the EO response for the PDLC with different proportion of E7/TMT.

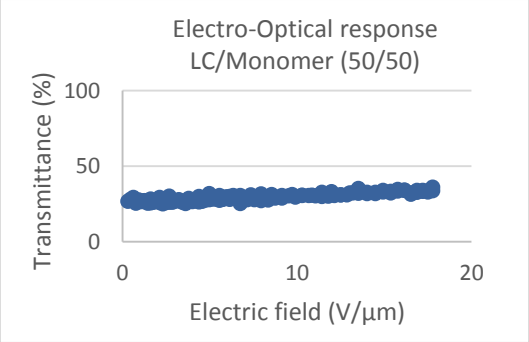


Figure III.1 - EO response for the E7/TMT (50/50)

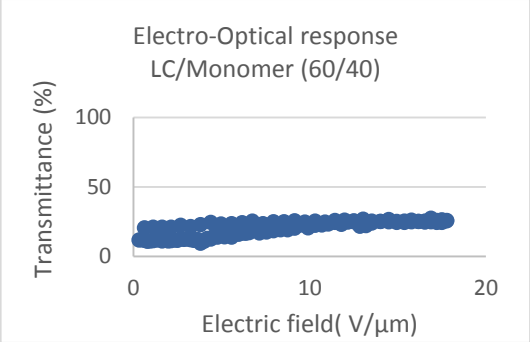


Figure III.2 - EO response for the E7/TMT (60/40)

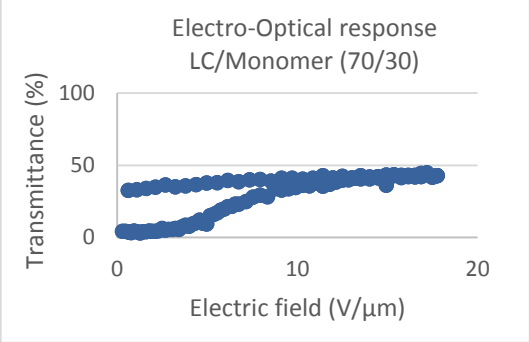


Figure III.3 - EO response for the E7/TMT (70/30)

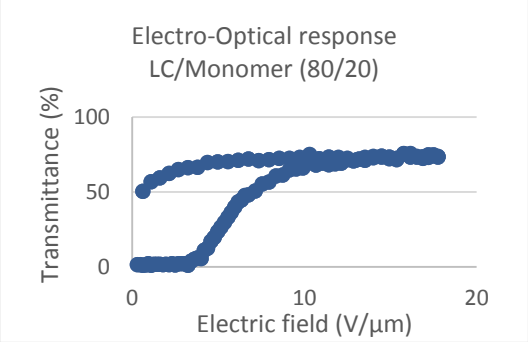


Figure III.4 - EO response for the E7/TMT (80/20)

Table III.1 show the main results for the EO response for different proportions of E7/TMT system.

Table III.1 - Resume for EO analysis E7/TMT

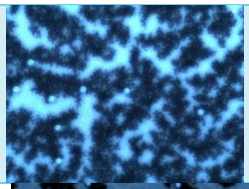
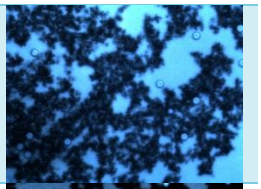
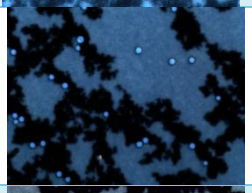
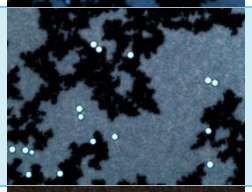
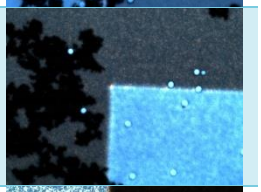
LC/TMT	Polymerization time	%C	%PME	Tmáx %	E90 V/µm	T0	Toff
50/50	1 day	-	-	32%	-	27%	29%
60/40	1 day	9%	69%	25%	9.5	12%	21%
70/30	1 day	29%	78%	41%	10.7	4%	33%
80/20	1 day	49%	68%	73%	9.9	1%	50%

Table III.1 shows that with the increase of the proportion of LC the initial transmittance (T_0) decreases and the final transmittance (T_{off}) increases, so the PDLC has an initial state more opaque and a final state more transparent with the increase of the proportion of LC.

3.1.2. Polarized Optical Microscopy

Table III.2 show the POM analysis for the different proportion of E7/TMT.

Table III.2 - POM analysis for the different proportions of E7/TMT

LC/Monomer	POM before EO	POM after EO
50/50		
60/40		
70/30		
80/20		

Through the POM images it is possible to observe black regions of no birefringent material, i.e., regions where only polymer exist. These images are taken using crossed polarizes, so all material that is no birefringent appears black.

Observing the POM images, it is possible to see the decline of the no birefringent zones with the increase of the LC. This decline explaine the increase of the maximum transmittance at the EO response.

3.2. Study of the PDLC made by PE4A polymer and E7 liquid crystal

Following the study, the next monomer studied is a tetra-acrylate monomer, the PE4A, which is a monomer with four polymerizable groups.

3.2.1. Electro Optical Response

Figure III.5, Figure III.6, Figure III.7 and Figure III.8 show the EO response for different proportions of E7/PE4A.

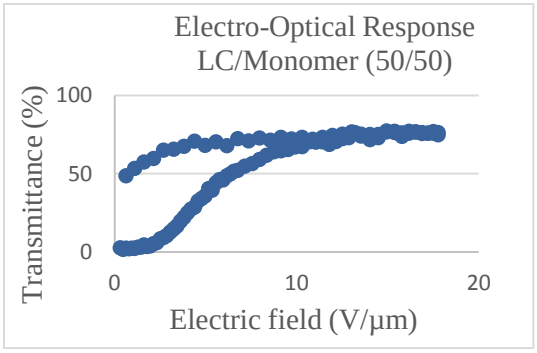


Figure III.5 - EO response for the E7/PE4A proportion 50/50

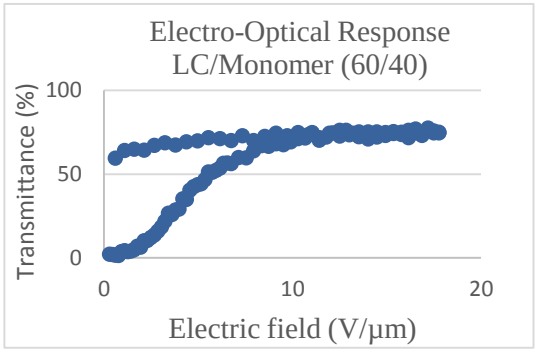


Figure III.6 - EO response for the E7/PE4A proportion 60/40

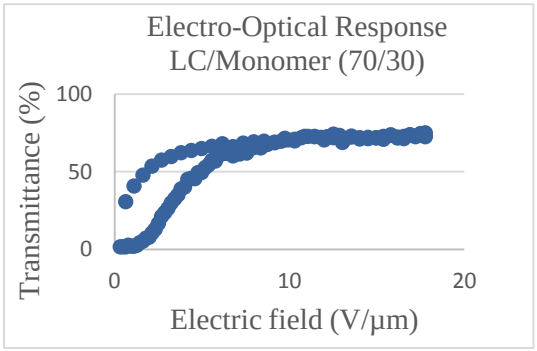


Figure III.7 - EO response for the E7/PE4A proportion 70/30

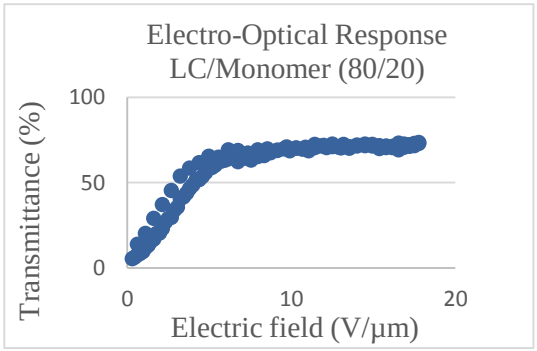


Figure III.8 - EO response for the E7/PE4A proportion 80/20

Table III.3 show the main results for the EO response for different proportions of E7/PE4A.

Table III.3 - Resume for EO analysis for E7/PE4A system

LC/PE4A	Polymerization time	%C	%PME	Tmáx %	E90 V/µm	T0	Toff	T_C
50/50	1 day	46%	63%	76%	10.25	3%	49%	61.2ºC
60/40	1 day	59%	80%	74%	8.7	0%	59%	59.9ºC
70/30	1 day	29%	43%	70%	7.5	1%	30%	59.4ºC
80/20	1 day	9%	14%	70%	6.75	5%	14%	60.3ºC

Through the EO response it is possible to conclude that the best LC/PE4A proportion is the 60/40 proportion. The permanent memory effect, for the 60/40 proportion, is 80%.

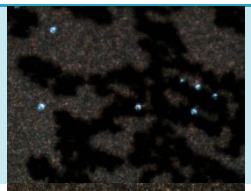
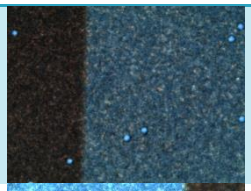
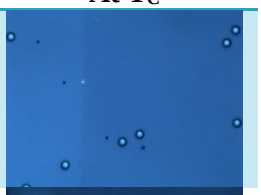
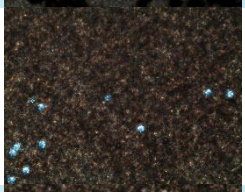
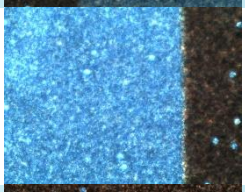
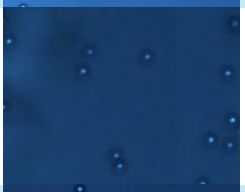
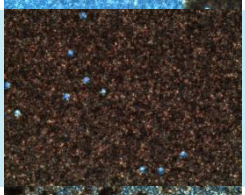
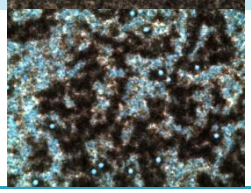
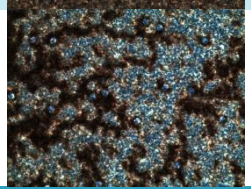
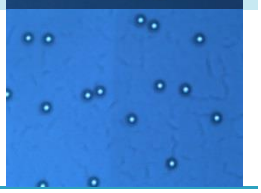
With the increases of the proportion of the PE4A in the mixture the E_{90} increases.

With the increases of proportion of E7 the micro domains of liquid crystal in the polymeric matrix increases and the anchorage force decrease, so the E90 decreases.

3.2.2. Polarized Optical Microscopy

Table III.4 show the POM analysis for the different E7/PE4A proportions.

Table III.4 - POM analysis for the different proportions of E7/PE4A

%E7	Before EO	After EO	At T_C
50%			
60%			
70%			
80%			

In Table III.4 it is possible to observe the appearance of no birefringent zones, that fact can be explained by the crosslink of the polymer network, because PE4A is a monomer with four polymerizable groups and forms polymeric networks very crosslinked.

3.3. Study of the PDLC using a co-polymerization made by PE4A and AP, and E7 liquid crystal

Due to a monomer with four polymerizable groups forms PDLCs with a polymeric network highly crosslinked, a co-polymerization with an oligomer with one polymerizable group was studied, in order to decrease the crosslinking.

Many combinations of E7/(PE4A/AP) were made and Figure III.9 show a graph that relates the variation of the permanent memory effect with the variation of the proportion of PE4A/AP.

All the EO analysis used to construct this graph are in the appendix chapter.

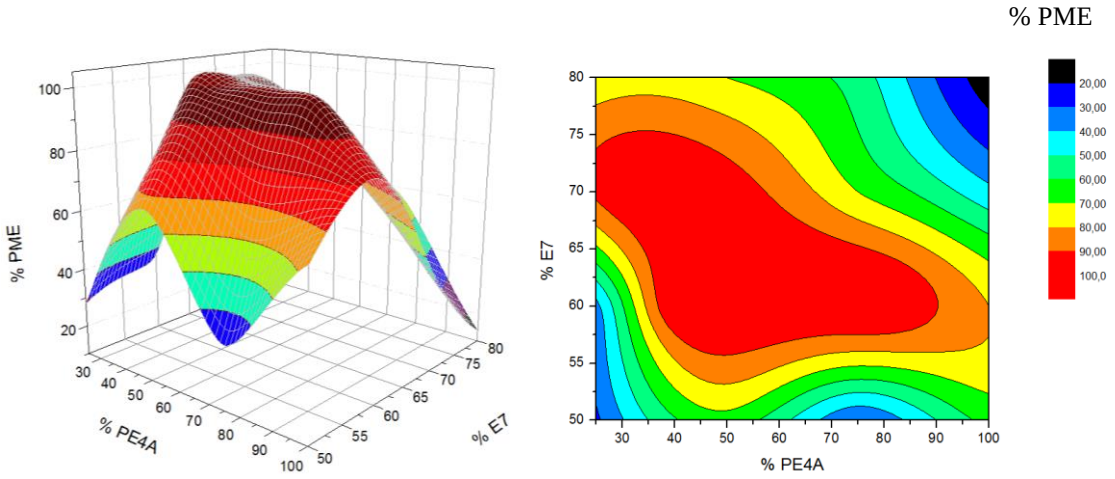


Figure III.9 – Variation of % PME with %E7 and %PE4A

In Figure III.9 is possible to observe an interval between 30% e 90% for PE4A where it is possible to achieve a good permanent memory effect, regarding for the liquid crystal the interval lies between 55% and 75%, this allows to conclude that the best percentage of liquid crystal to work it is 60%, with 40-80% to produce PDLCs with 100% of PME. There is no reference in bibliography for a higher PME such as this.

This chapter will speak only about the percentage of liquid crystal which is 60%.

3.3.1. Electro Optical Response

Figure III.10, Figure III.11, Figure III.12 and Figure III.13 show the EO response for different proportions of PE4A/AP.

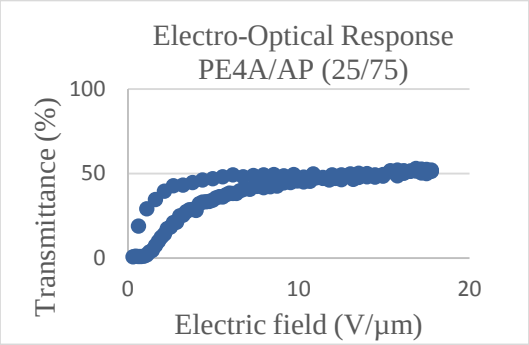


Figure III.10 - EO response for the percentage of E7 of 60% and PE4A/AP proportion of 25/75

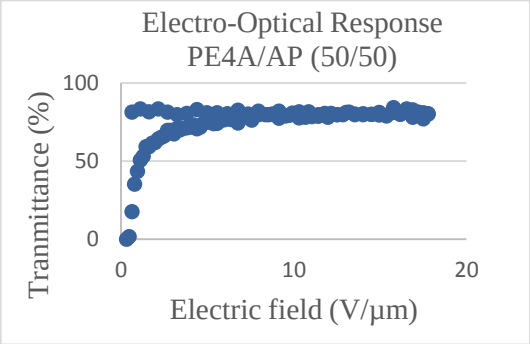


Figure III.11 - EO response for the percentage of E7 of 60% and PE4A/AP proportion of 50/50

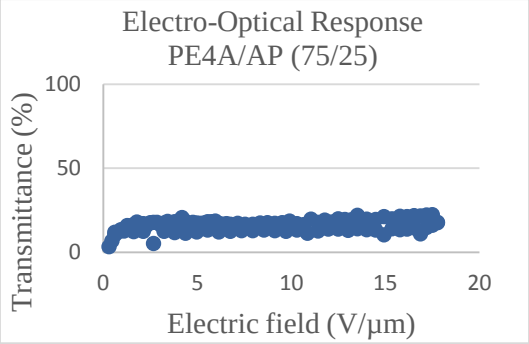


Figure III.12 - EO response for the percentage of E7 of 60% and PE4A/AP proportion of 75/25

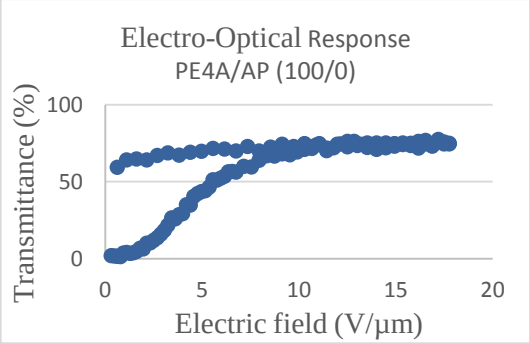


Figure III.13 - EO response for the percentage of E7 of 60% and PE4A/AP proportion of 100/0

Table III.5 show the main conclusions obtained by observing the electro-optical response.

Table III.5 - Results of EO analysis for the percentage of E7 of 60% and the different proportions of PE4A/AP

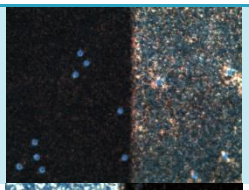
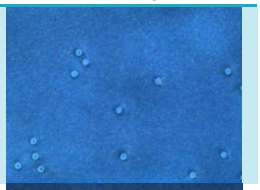
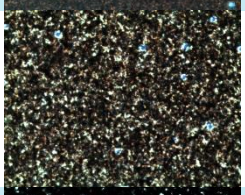
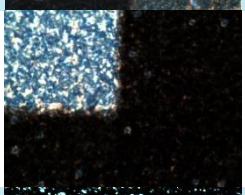
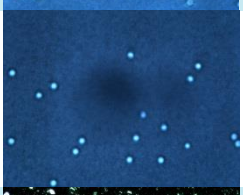
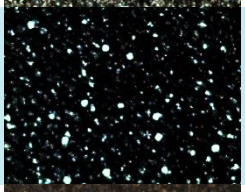
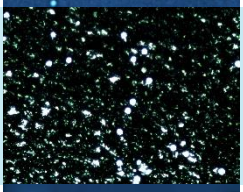
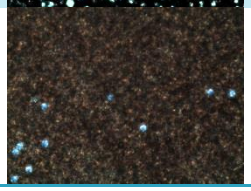
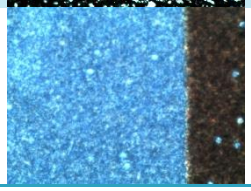
PE4A/AP	Polymerization time	%C	%PME	Tmax	E90 V/µm	T0	Toff	T_C
25/75	1 day	19%	37%	52%	4.95	0%	19%	49.2ºC
50/50	1 day	76%	100%	85%	4.35	9%	85%	55.2ºC
75/25	1 day	-	-	18%	-	3%	12%	54.7ºC
100/0	1 day	59%	80%	74%	8.7	0%	59%	59.9ºC

In Table III.5 it is possible to conclude that the best proportion of PE4A/AP is 50/50 for 60% of E7.

3.3.2. Polarized Optical Microscopy

Table III.6 show the POM analysis for the different proportions of PE4A/AP.

Table III.6 - POM analysis for the different proportions of PE4A/AP

PE4A/AP	%E7	Before EO	After EO	At T_c
25/75	60%			
50/50	60%			
75/25	60%			
100/0	60%			

By the POM analysis is possible to observe that in proportion 75/25 of PE4A/AP there is many no birefringent material regions, that explains the EO response for this sample.
This is due to the crosslinked of the polymer network.

3.3.3. Scanning Electron Microscopy

Figure III.14 and Figure III.15 show the SEM analysis for the PE4A/AP proportion of 50/50.

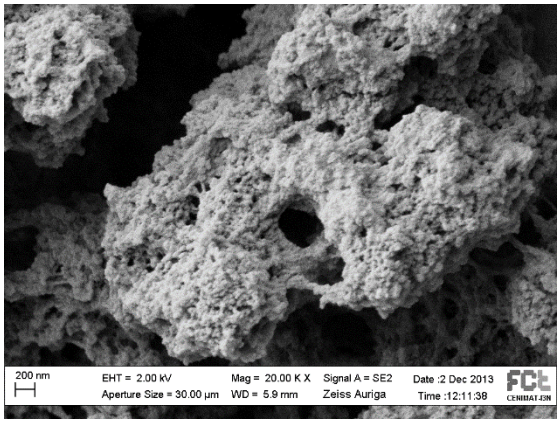


Figure III.14 - SEM analysis for 60% of E7 and PE4A/AP proportion of (50/50) (Magnification of 20000 and 1 day of polymerization)

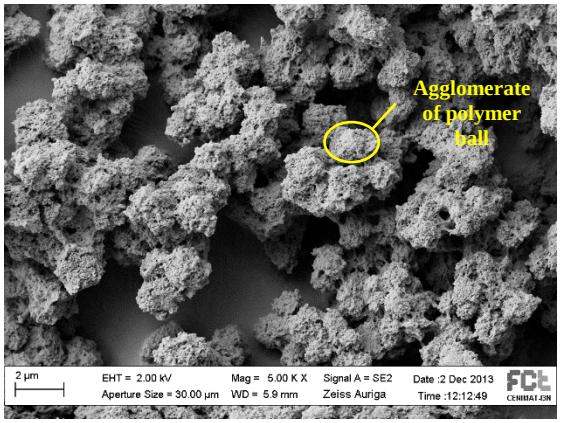


Figure III.15 - SEM analysis for 60% of E7 and PE4A/AP proportion of (50/50) (Magnification of 5000 and 1 day of polymerization)

By the images showed above it is possible to conclude that the polymer network struture is polymer ball type, and an polymer ball agglomerate showed a size between 1 µm and 2 µm. By observing the images, is not possible to measure the exact size of the polymer ball but its dimension is between 10-50 nm.

The same analysis was made for a sample with 3 days of polymerization and the structure is the same. Those images are in the appendix chapter.

Figure III.16 and Figure III.17 show the SEM analysis for the PE4A/AP proportion of 75/25.

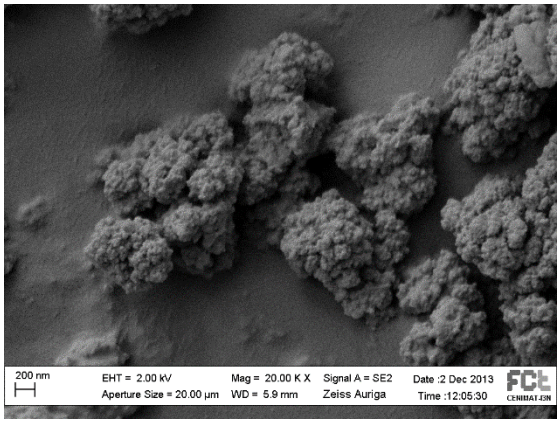


Figure III.16 - SEM analysis for 60% of E7 and PE4A/AP proportion of (75/25) (Magnification of 20000 and 1 day of polymerization)

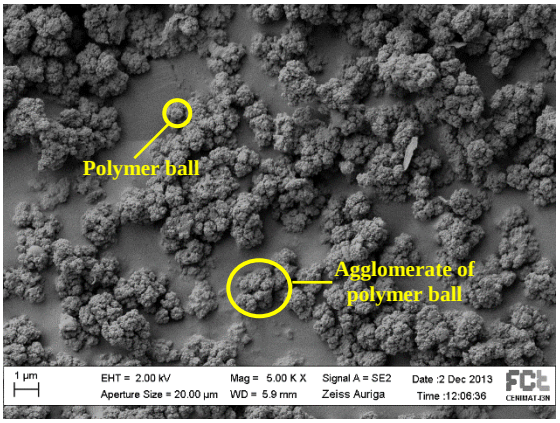


Figure III.17 - SEM analysis for 60% of E7 and PE4A/AP proportion of (75/25) (Magnification of 5000 and 1 day of polymerization)

By the images showed above it is possible to conclude that the polymer network struture is polymer ball type, and an polymer ball agglomerate showed a size between 1.5 µm and 2 µm and a polymer ball has the size of, approximatly, 50 nm.

The same analysis was made for a sample with 2 days of polymerization and the structure is the same. Those images are in the appendix chapter.

Figure III.18 and Figure III.19 show the SEM analysis for the PE4A/AP proportion of 100/0

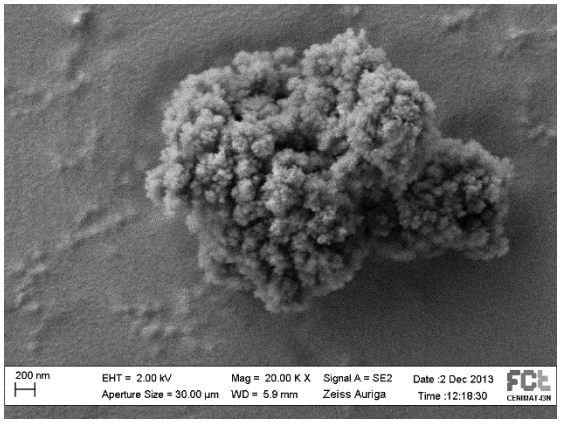


Figure III.18 - SEM analysis for 60% of E7 and PE4A/AP proportion of (100/0) (Magnification of 20000 and 1 day of polymerization)

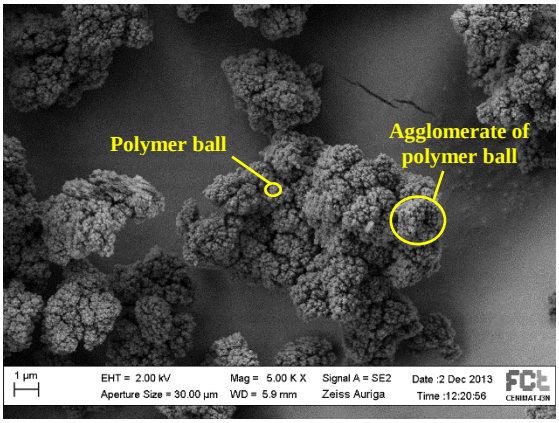


Figure III.19 - SEM for 60% of E7 and PE4A/AP proportion of (100/0) (Magnification of 5.000 and 1 day of polymerization)

By the images showed above it is possible to conclude that the polymer network struture is polymer ball type, and an polymer ball agglomerate showed a size between, 0.5 µm and 3 µm and a polymer ball has the size between, approximatly,50. nm and 70 nm.

The same analysis was made for a sample with 2 days of polymerization and the structure is the same. Those images are in the appendix chapter.

3.3.4. Differential Scanning Calorimetry

In order to determine the T_g of the monomers/oligomers, the T_g of the polymers, the T_g of a mixture, the nematic isotropic temperature of the liquid crystal E7 and the nematic isotropic temperature of the liquid crystal E7 in the polymeric film of a PDLC, DSC analysis were performed.

In the DSC analysis a sample of known mass was heating and cooled at a known speed, the velocity of heating was 5ºC/min and the velocity of cooling was 10ºC/min.

- ✓ AP

Figure III.20 and Figure III.21 show the two DSC heating cycles for oligomer AP.

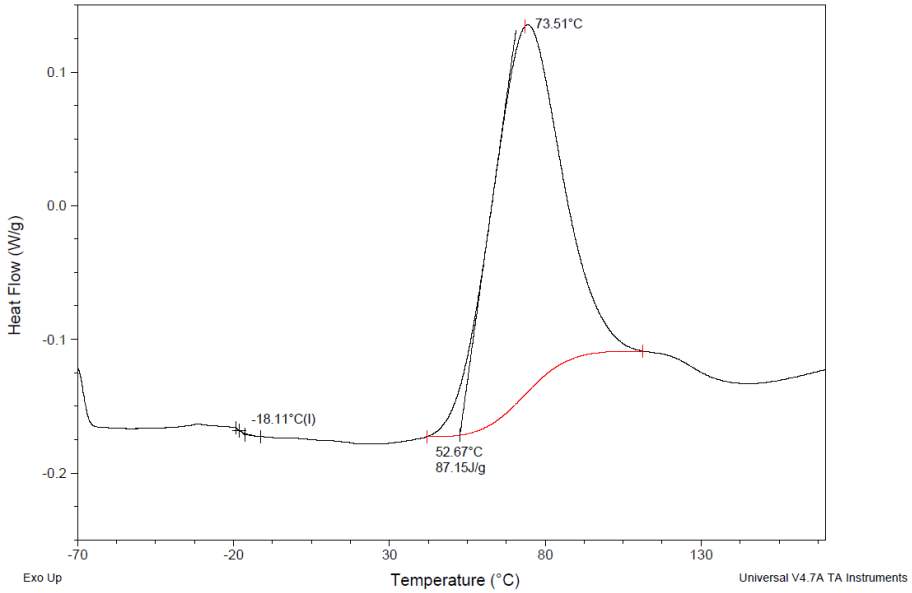


Figure III.20 - DSC first heating cycle for AP

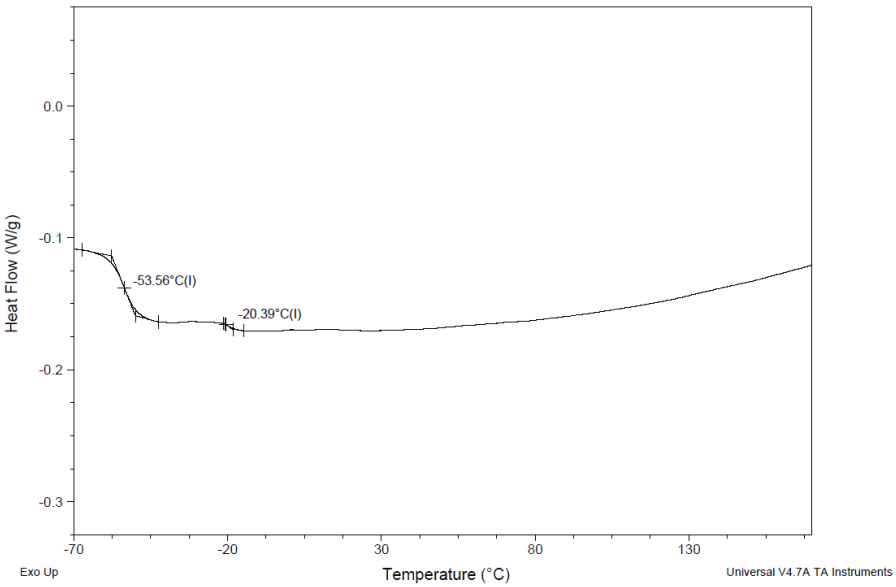


Figure III.21 - DSC second heating cycle for AP

In the first cycle it is possible to observe the polymerization of the oligomer and the T_g of oligomer at -18.11ºC.

The second and the third cycles, show the DSC of the polymer AP and it is possible to observe the T_g related to the polymer at -53.36ºC and the T_g related to the leftover of the oligomer which was not polymerized at -20.39ºC.

A third heating cycle was made, the results were the same as for the second cycle.

- ✓ PE4A

Figure III.22 and Figure III.23 show the two DSC heating cycles for monomer PE4A.

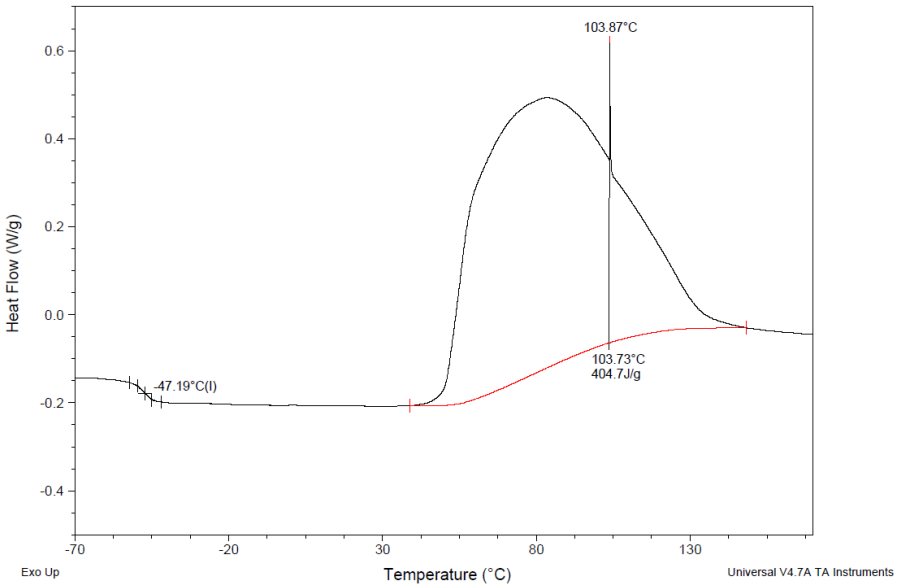


Figure III.22 - DSC first heating cycle for PE4A

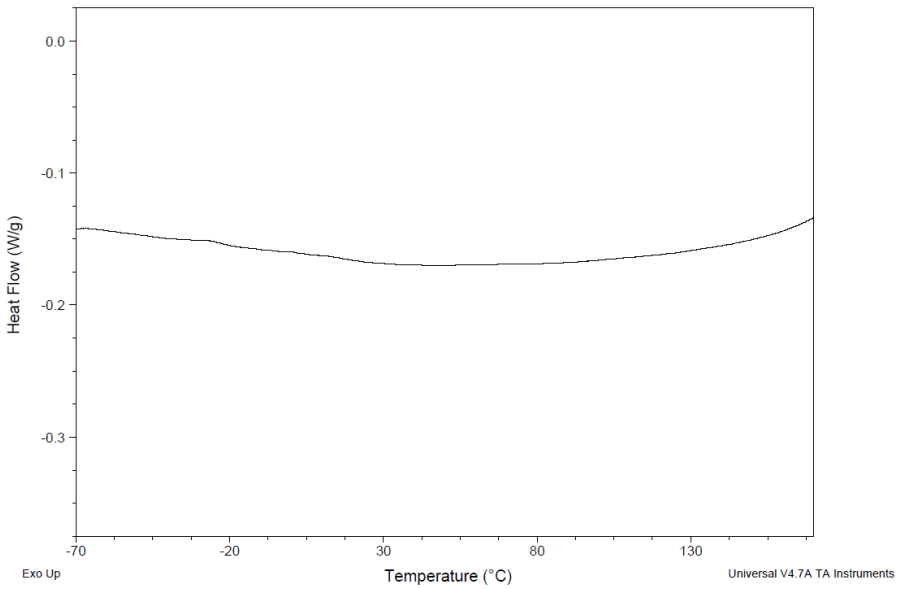


Figure III.23 - DSC second heating cycle for PE4A

In the first cycle it is possible to observe the polymerization of the monomer and the T_g of monomer at -47.19ºC.

The second cycle show the DSC of the polymer PE4A and no PE4A polymer T_g was detected, although it was found in literature at 180ºC. [33]

A third heating cycle was made, the results are the same as for the second cycle.

- ✓ PE4A/AP (50/50)

Figure III.24 and Figure III.25 show the two DSC heating cycles for co-polymerization PE4A/AP (50/50).

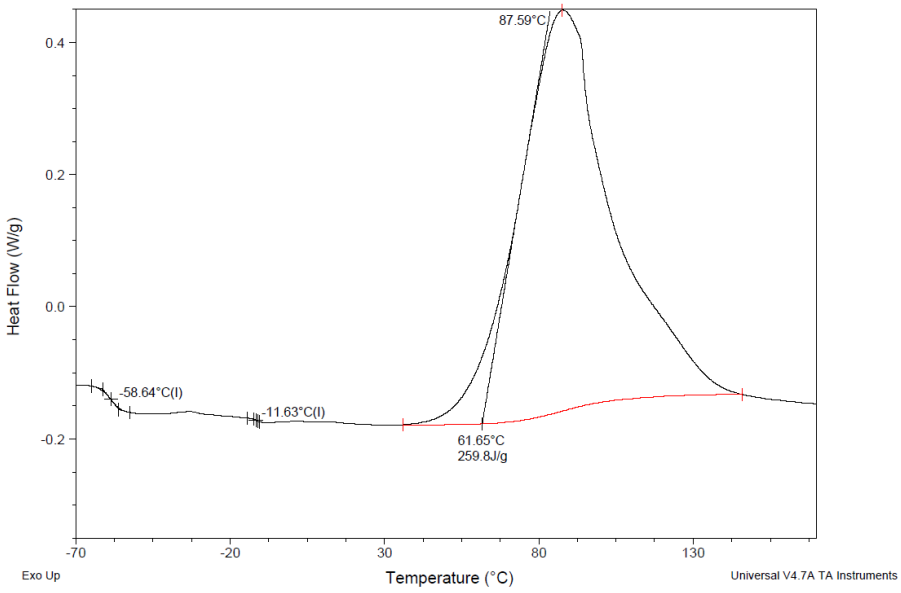


Figure III.24 - DSC first heating cycle for PE4A/AP (50/50)

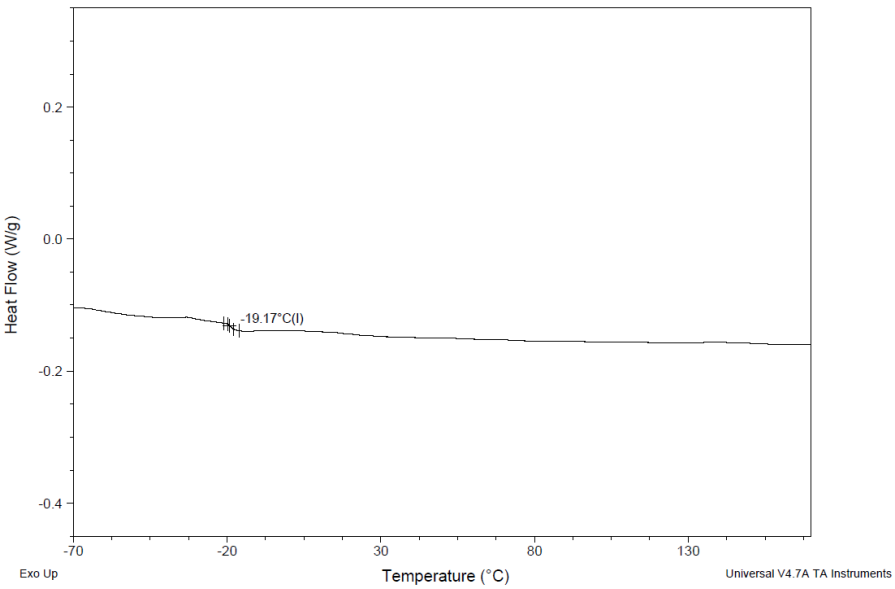


Figure III.25 - DSC second heating cycle for PE4A/AP (50/50)

In the first cycle it is possible to observe the polymerization of the solution and it can be observed two different T_g's, the first at -58.64ºC and this value correspond to T_g of the monomer PE4A and the second at -11.63ºC and this value correspond to T_g of the oligomer AP. The second cycle show the DSC of the co-polymerized PE4A/AP (50/50) and it is only possible to observe one T_g at -19.17, probably corresponding to some AP oligomer, that was not polymerized in the first cycle.

A third heating cycle was made, the results were the same as for the second cycle.

- ✓ E7

Figure III.26 and Figure III.27 show the two DSC heating cycles for E7 liquid crystal.

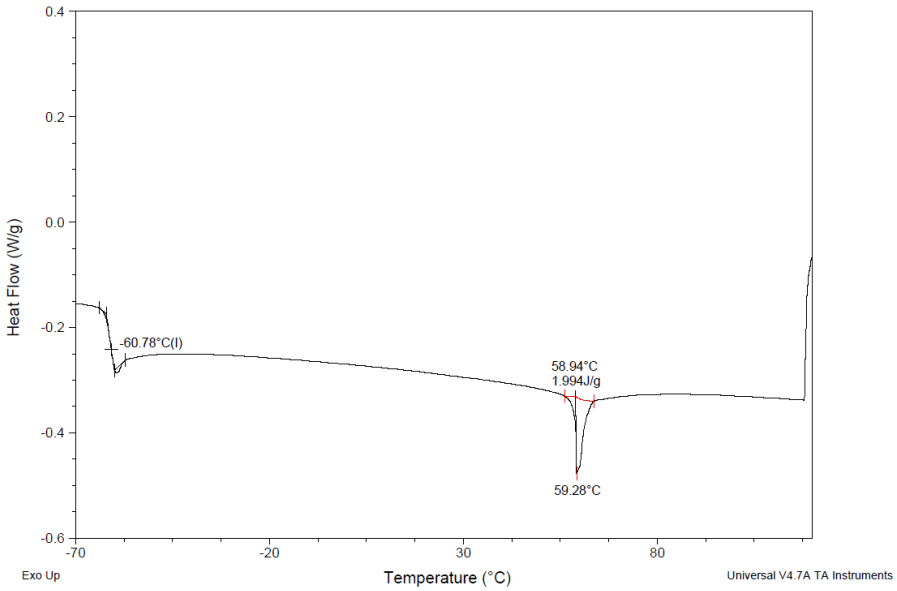


Figure III.26 - DSC first heating cycle for E7

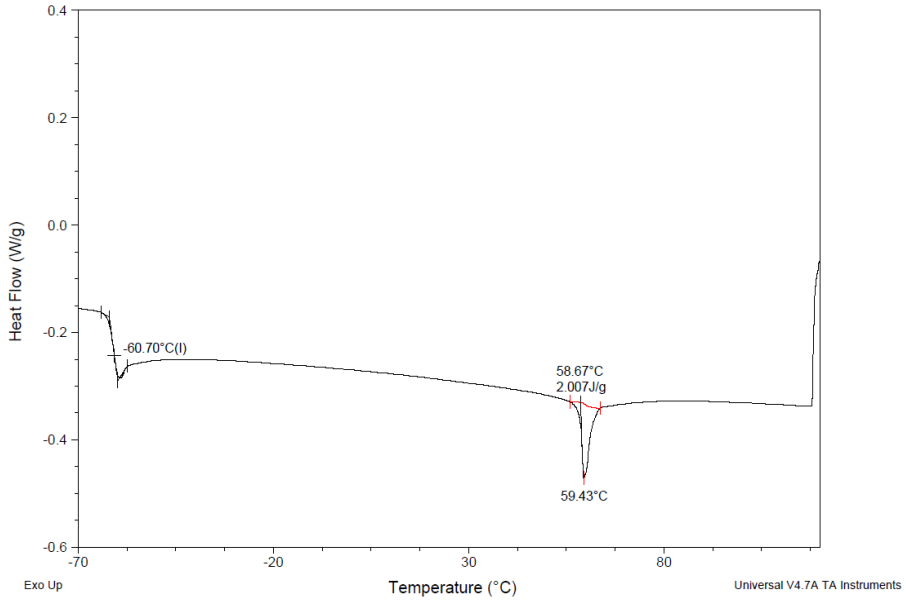


Figure III.27 - DSC second heating cycle for E7

In the two cycles it is possible to observe the T_g of E7 liquid crystal at -60.7ºC and the nematic isotropic temperature (T_{NI}) at 59.3-59.4ºC

- ✓ PDLC using a co-polymerization made PE4A and AP, and E7 liquid crystal

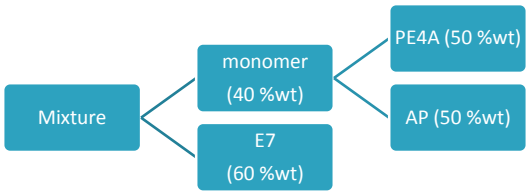


Figure III.28 and Figure III.29 show the two DCS heating cycles for the PDLC using a co-polymerization made PE4A and AP, and E7 liquid crystal

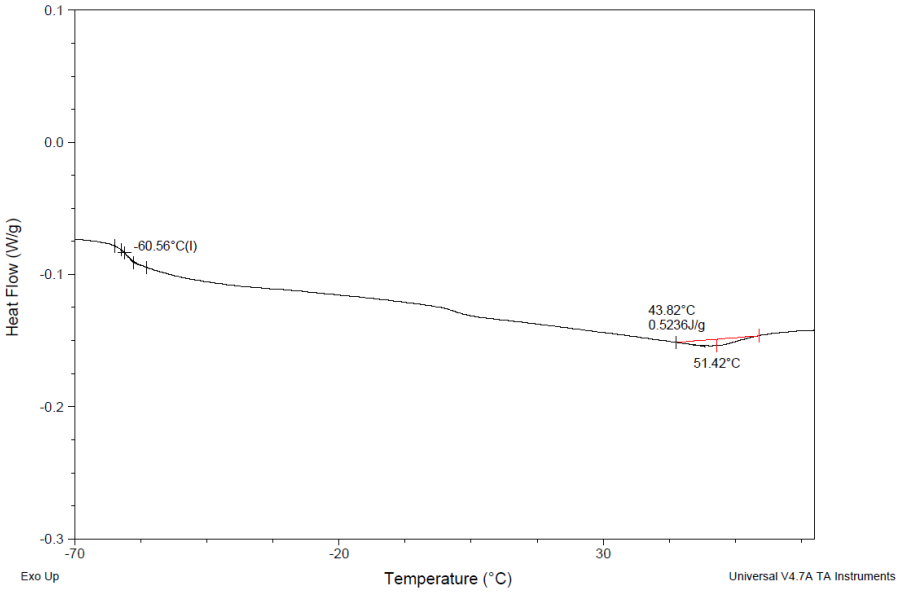


Figure III.28 - DSC first heating cycle for the mixture

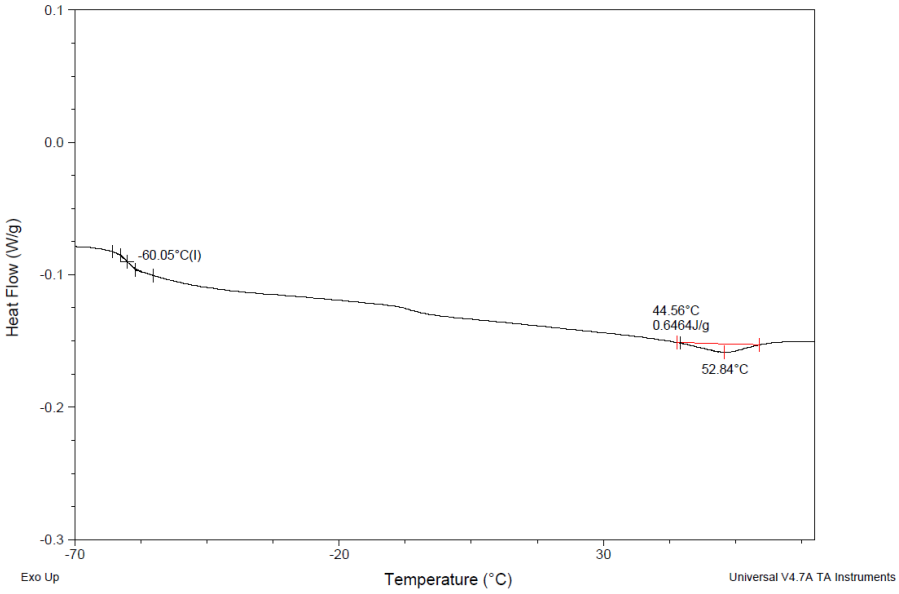


Figure III.29 - DSC second heating cycle for the mixture

In two cycles it is possible to observe a T_g at -60.56ºC, that T_g corresponds to the T_g of LC E7. It is possible to observe the T_{NI} of liquid crystal in the PDLC film at 52.84ºC.

3.3.5. Viscosity measurements

Viscosity measurements were made to verify if the increase of the viscosity of the monomer mixtures could influence the polymerization.

Figure III.30, Figure III.31, Figure III.32, Figure III.33 and Figure III.34 show the variation of viscosity for the different PE4A/AP proportions.

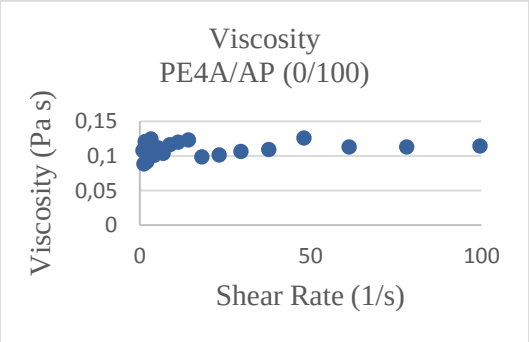


Figure III.30 - Viscosity variation for PE4A/AP (0/100)

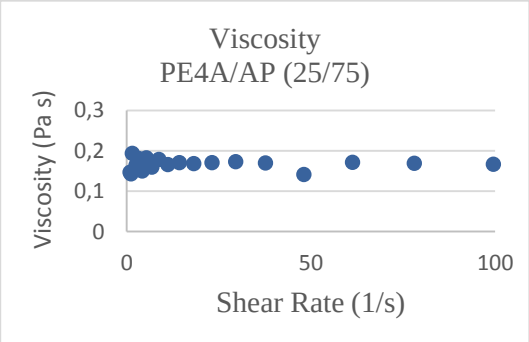


Figure III.31 - Viscosity variation for PE4A/AP (25/75)

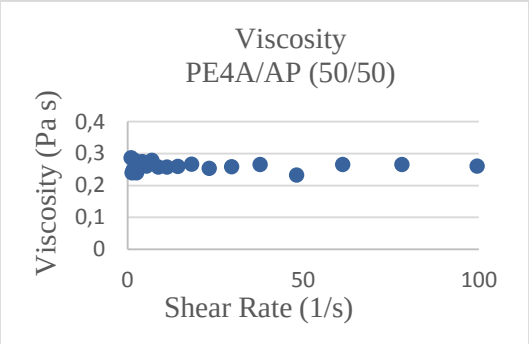


Figure III.32 - Viscosity variation for PE4A/AP (50/50)

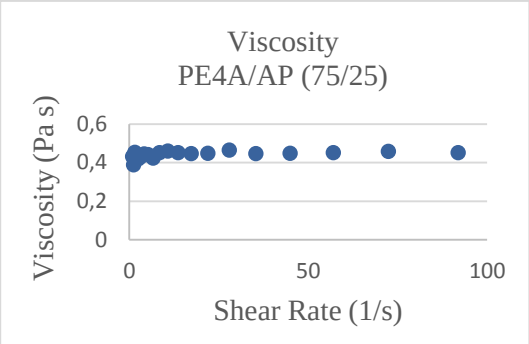


Figure III.33 - Viscosity variation for PE4A/AP (75/25)

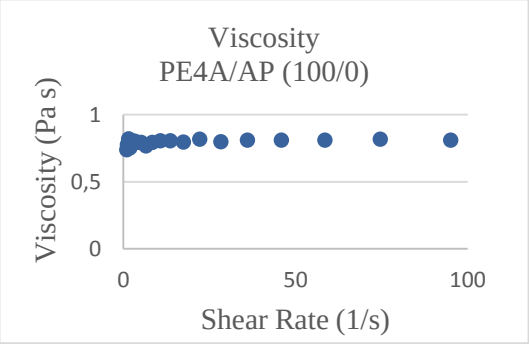


Figure III.34 - Viscosity variation for PE4A/AP (100/0)

Table III.7 show the results of the viscosity measurements. It is possible to observe an increase of the viscosity with the increase of the monomer PE4A percentage, due to the higher value of the viscosity of this monomer.

Table III.7 - Resume of the viscosity measurements

PE4A/AP	Viscosity (Pa s)
0/100	0.1
25/75	0.17
50/50	0.26
75/25	0.45
100/0	0.8

With a more viscous monomer the kinetic of the polymerization reaction decreases due to the hindrance of movements, so with 100% of PE4A the kinetic of the polymerization reaction is slower. Nevertheless, no relationship between the monomer/oligomer viscosity and final polymer structure was found.

3.3.6. *Polymerization time study*

It was necessary to study the polymerization time dependence because some cells presented after some polymerization time no birefringent regions, that caused a decrease of the transmittance and it was impossible render the cell transparent.

In the following graphs T_x represents the time for the x minutes of polymerization.

3.3.6.1. *System with PE4A/AP proportion of 25/75 and 60% of E7 liquid crystal*

Figure III.35 show, for different polymerization time, the EO analysis for PE4A/AP proportion of 25/75.

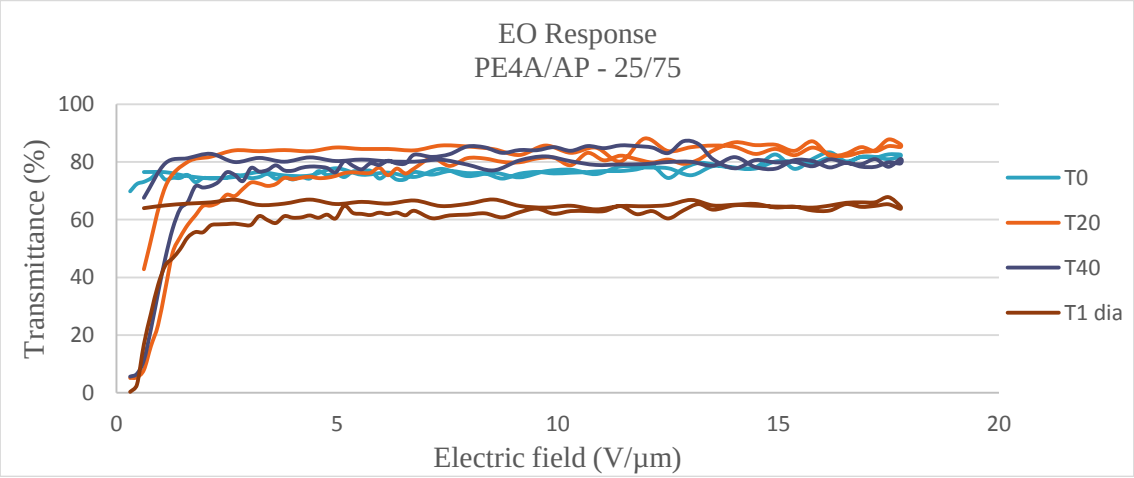


Figure III.35 - Variation of the EO response for the different polymerization times for the percentage of E7 of 60% and PE4A/AP (25/75)

Figure III.36 show the variation of the permanent memory effect and the percentage of memory state contrast with polymerization time.

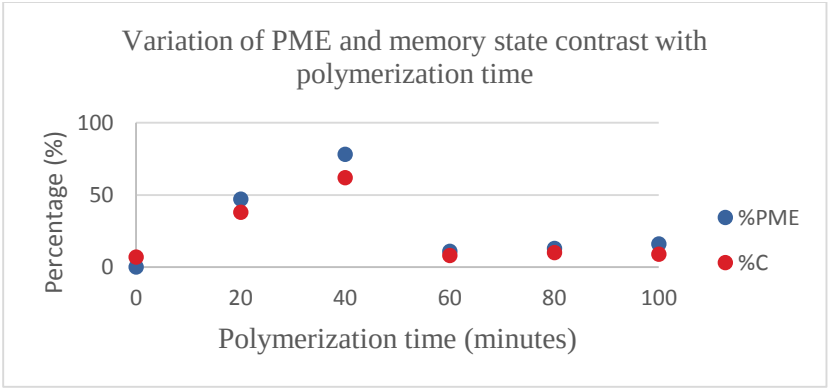
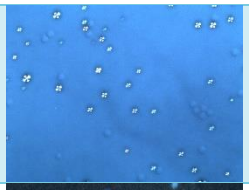


Figure III.36 - Variation of the permanent memory effect and memory state contrast with polymerization time for the PE4A/AP proportion of 25/75

Table III.8 show the POM analysis for different polymerization times for the PE4A/AP proportion of 25/75 in PDLC systems incorporating 60% of E7 liquid crystal.

Table III.8 - Variation of the POM analysis for the different polymerization times for 60% of E7 and PE4A/AP (25/75)

Polymerization time	Before EO	After EO
0 minutes		
20 minutes		
40 minutes		
1 day		

By EO analysis, POM analysis and Figure III.36, it is possible to choose the optimal polymerization time. For PE4A/AP (25/75), the optimal polymerization time is 40 minutes were obtained 78% of permanent memory effect and memory state contrast is 62%.

3.3.6.2. System with PE4A/AP proportion of 50/50 and 60% of E7 liquid crystal

Figure III.37 show, for different polymerization times, the EO analysis for PE4A/AP proportion of 50/50.

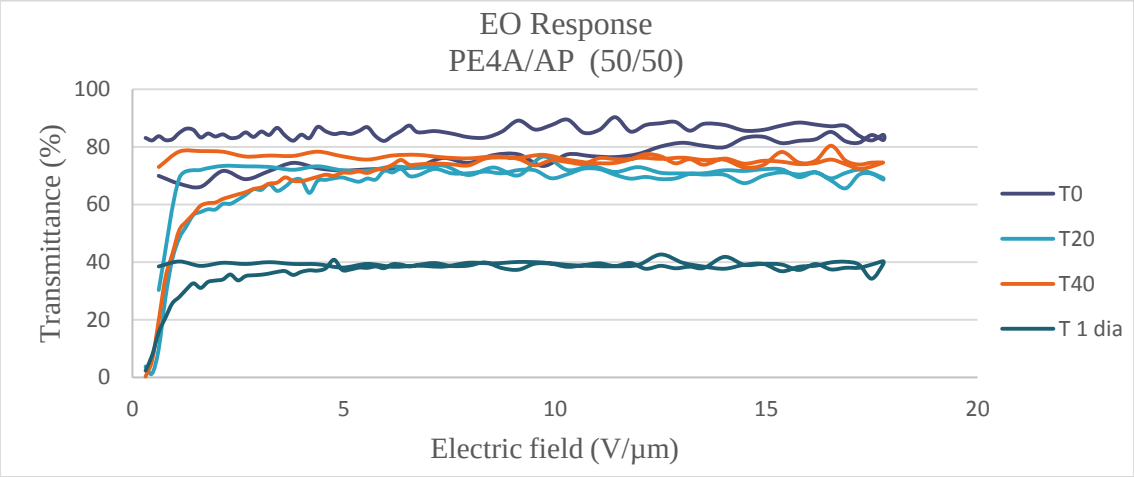


Figure III.37 - Variation of the EO response for the different polymerization times for the percentage of E7 of 60% and PE4A/AP (50/50)

Figure III.38 show the variation of the permanent memory effect and the percentage of memory state contrast with polymerization time.

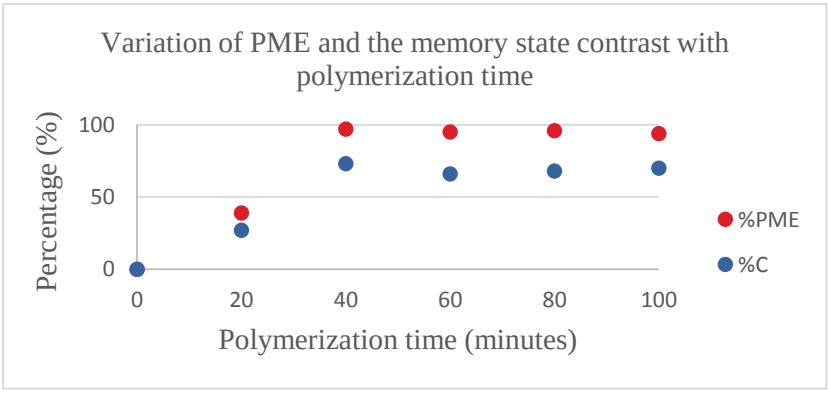


Figure III.38 - Variation of the permanent memory effect and memory state contrast with polymerization time for the PE4A/AP proportion of 50/50

Table III.9 show the POM analysis for different polymerization times for the PE4A/AP proportion of 50/50, in PDLC systems incorporating 60% of E7 liquid crystal.

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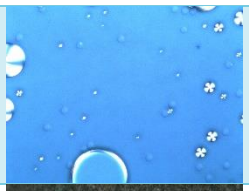
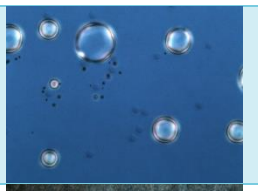
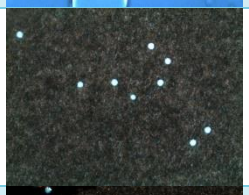
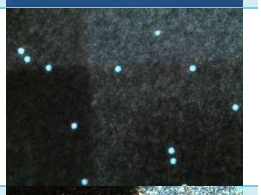
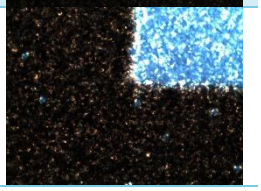
Table III.9 - Variation of the POM analysis for the different polymerization times for the percentage of LC of 60% and PE4A/AP (50/50)

Polymerization time	Before EO	After EO
0 minutes		
20 minutes		
40 minutes		
1 day		

By EO analysis, POM analysis and Figure III.38, it is possible to choose the optimal polymerization time. For PE4A/AP (50/50), the optimal polymerization time is 40 minutes, were obtained 98% of permanent memory effect and memory state contrast is 73%.

3.3.6.3. System with PE4A/AP proportion of 75/25 and 60% of E7liquid crystal

Figure III.39 show, for different polymerization time, the EO analysis for PE4A/AP proportion of 75/25.

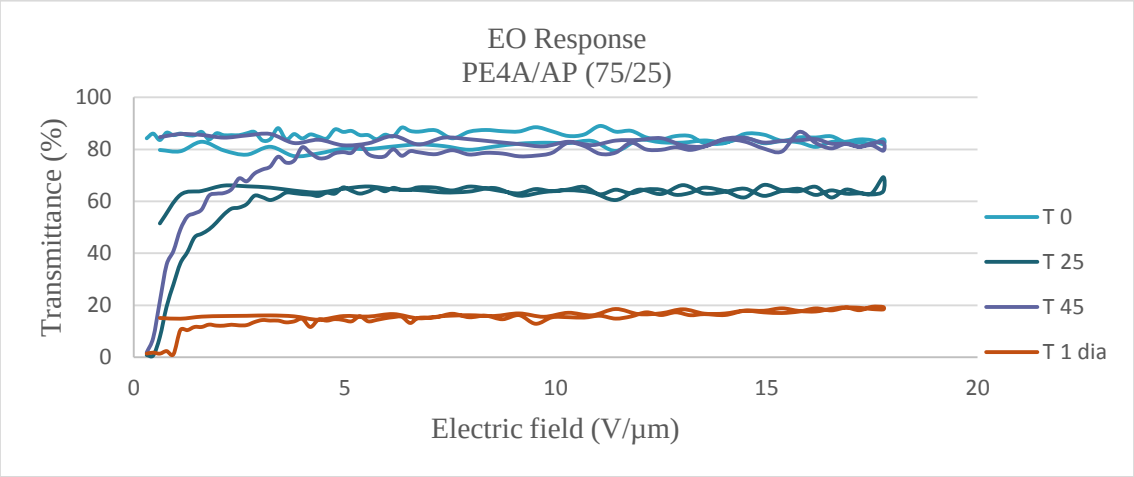


Figure III.39 - Variation of the EO response for the different polymerization times for the percentage of E7 of 60% and PE4A/AP (75/25)

Figure III.40 show the variation of the permanent memory effect and the memory state contrast with polymerization time.

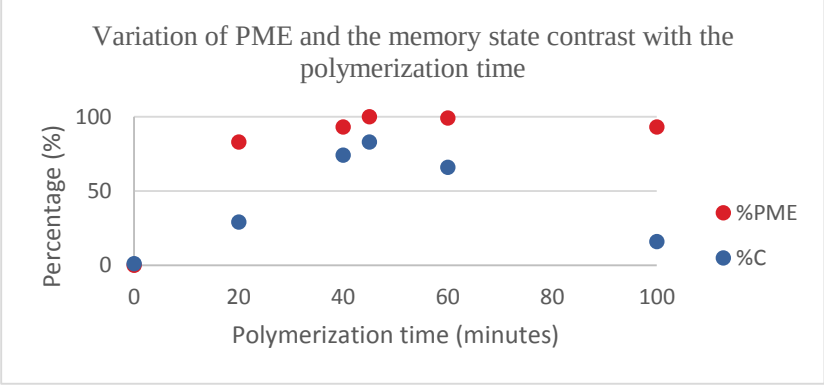
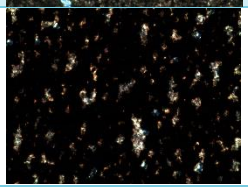
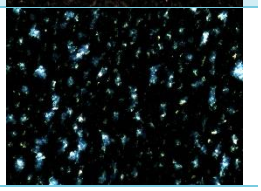


Figure III.40 - Variation of the permanent memory effect and memory state contrast with polymerization time for the PE4A/AP proportion of 75/25

Table III.10 show the POM analysis for different polymerization times for PE4A/AP proportion of 75/25, in PDLC systems incorporating 60% of E7 liquid crystal.

Table III.10 - Variation of the POM analysis for the different polymerization times for the percentage of LC of 60% and PE4A/AP (75/25)

Polymerization time	Before EO	After EO
0 minutes		
25 minutes		
45 minutes		
1 day		

By EO analysis, POM analysis and Figure III.40, it is possible to choose the optimal polymerization time. For PE4A/AP (75/25), the optimal polymerization time is 45 minutes, were obtained 100% of permanent memory effect and memory state contrast is 83%.

3.3.6.4. System with PE4A/AP proportion of 100/0 and 60% of E7 liquid crystal

Figure III.41 show, for different polymerization times, the EO analysis for PE4A/AP proportion of 100/0.

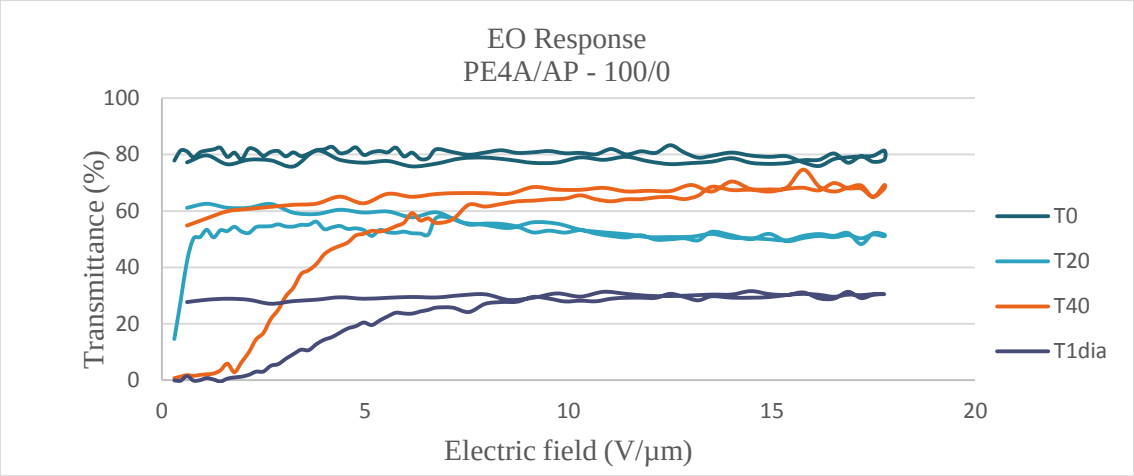


Figure III.41 - Variation of the EO response for the different polymerization times for the percentage of E7 of 60% and PE4A/AP (100/0)

Figure III.42 show the variation of the permanent memory effect and memory state contrast with polymerization time.

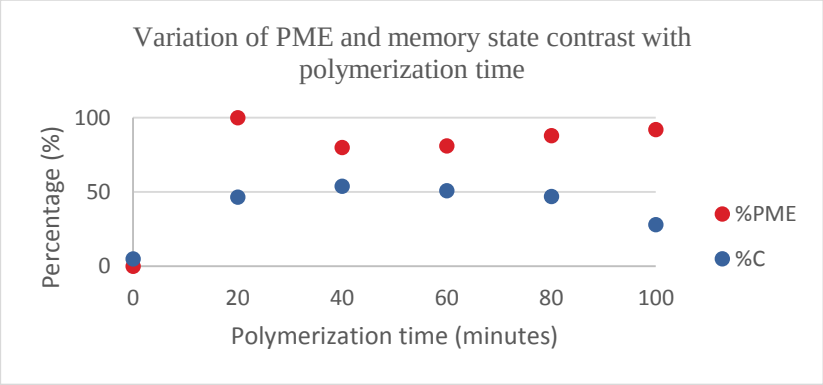
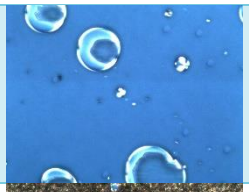
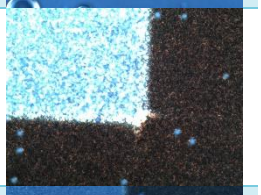


Figure III.42 - Variation of the permanent memory effect and memory state contrast with polymerization time for the PE4A/AP proportion of 100/0

Table III.11 show the POM analysis for different polymerization time for PE4A/AP proportion of 100/0, in PDLC systems incorporating 60% of E7 liquid crystal.

Table III.11 - Variation of the POM analysis for the different polymerization times for the percentage of LC of 60% and PE4A/AP (100/0)

Polymerization time	Before EO	After EO
0 minutes		
20 minutes		
40 minutes		
1 day		

By EO analysis, POM analysis and Figure III.42, it is possible to choose the optimal polymerization time. For PE4A/AP (100/0), the optimal polymerization time is 40 minutes, were obtained 80% of permanent memory effect and memory state contrast is 54%.

3.3.7. Optimal polymerization time

Through the results obtained in chapter 3.3.6. it is possible to choose the optimal polymerization time for the different PE4A/AP proportions and the EO study for those times was made.

Figure III.43, Figure III.44, Figure III.45 and Figure III.46 show the EO response for the different proportions of PE4A/AP with the optimal polymerization time.

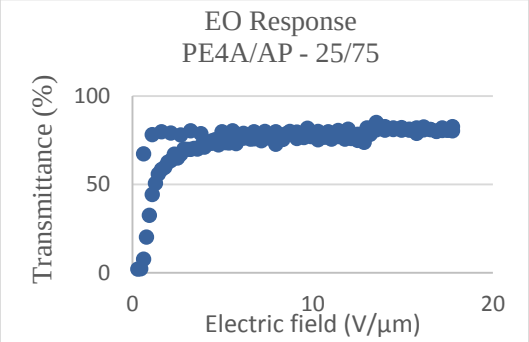


Figure III.43 - EO response for polymerization time of 40 minutes, for the percentage of E7 of 60% and PE4A/AP (25/75)

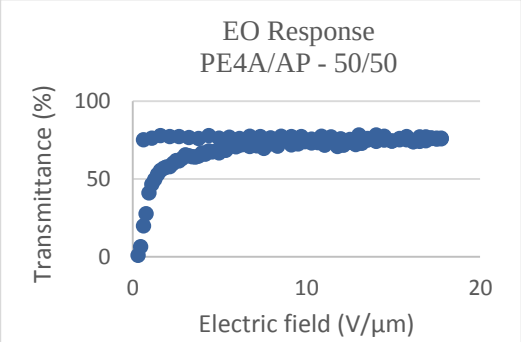


Figure III.44 - EO response for polymerization time of 40 minutes, for the percentage of E7 of 60% and PE4A/AP (50/50)

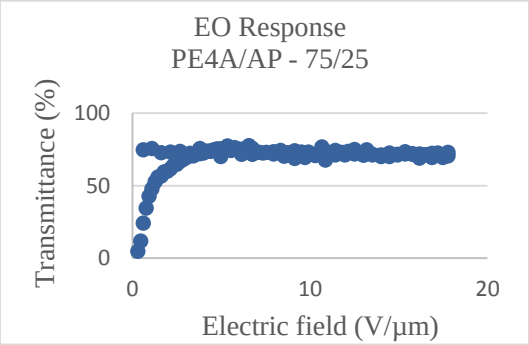


Figure III.45 - EO response for polymerization time of 45 minutes, for the percentage of E7 of 60% and PE4A/AP (75/25)

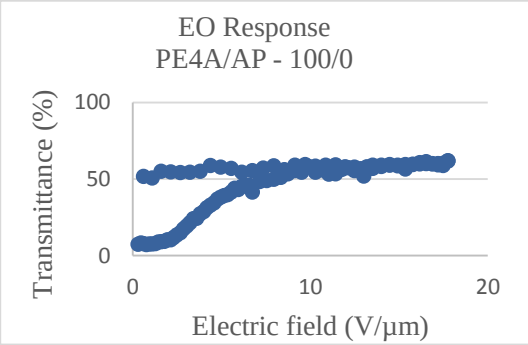


Figure III.46 - EO response for polymerization time of 40 minutes, for the percentage of E7 of 60% and PE4A/AP (100/0)

Table III.12 show the principals results for the EO response, for the different PE4A/AP proportions with the optimal polymerization time.

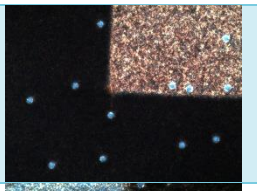
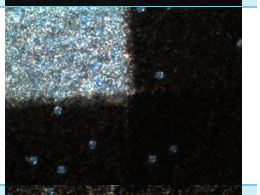
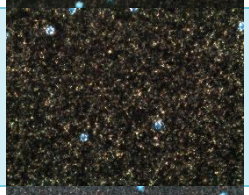
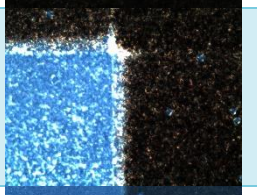
Table III.12- Resume of EO response for the percentage of E7 of 60% and the different PE4A/AP proportion at optimal polymerization time

PE4A/AP	Polymerization time	%C	%PME	Tmáx %	E90 V/µm	T0	Toff
25/75	40 Minutes	65%	83%	80%	3.8	2%	67%
50/50	40 Minutes	75%	98%	77%	6	1%	76%
75/25	45 Minutes	75%	100%	75%	2.9	5%	75%
100/0	40 Minutes	45%	86%	59%	8.7	7%	52%

By Table III.12 it is possible to observe that the PME of all the PE4A/AP proportions is high, to the PE4A/AP (50/50) and (75/25) the PME is 98% and 100% respectively. The system choose the scale-up is the system with PE4A/AP of 50/50, this system has 98% of PME. Was not chosen the system with PE4A/AP of 75/25 because a little variation of the polymerization time can lead to the appearance of no birefringent regions.

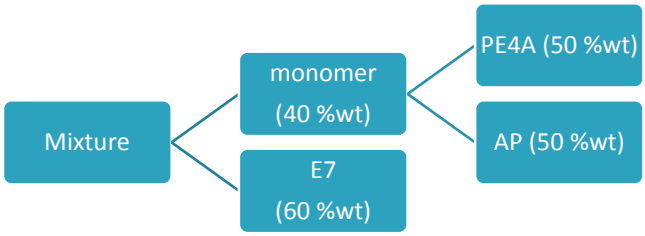
Table III.13 show the POM analysis for different PE4A/AP proportions with the optimal polymerization time.

Table III.13 – POM analysis for the percentage of LC of 60% and different PE4A/AP proportion at optimal polymerization time

PE4A/AP	Polymerization time	Before EO	After EO
25/75	40 minutes		
50/50	40 minutes		
75/25	45 minutes		
100/0	40 minutes		

3.4. . Scale-up in self-made cells

Scale up was made after the previous experimental results and after the choice of the best system. The best system are the co-polymerization with the next characteristics:



The optimal polymerization time was 40 minutes.

The scale-up was made in self-made, this cells are built with two conductive glasses, 2.5cm X 2cm, with polyimide alignment layer.

The spacing between the two glasses of 23 µm, was achieved by using strips of mylar.

Figure III.47 show the schematic illustration of the produced cells used in the scale-up.

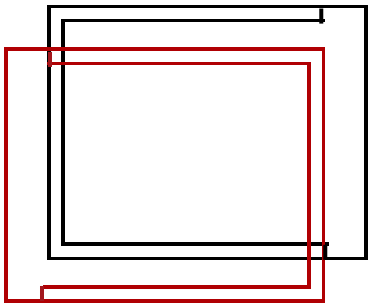


Figure III.47 - Schematic illustration for the cell

3.4.1. Electro Optical Response for the Scale-up Cells

Figure III.48 show the EO response for the scale-up cell.

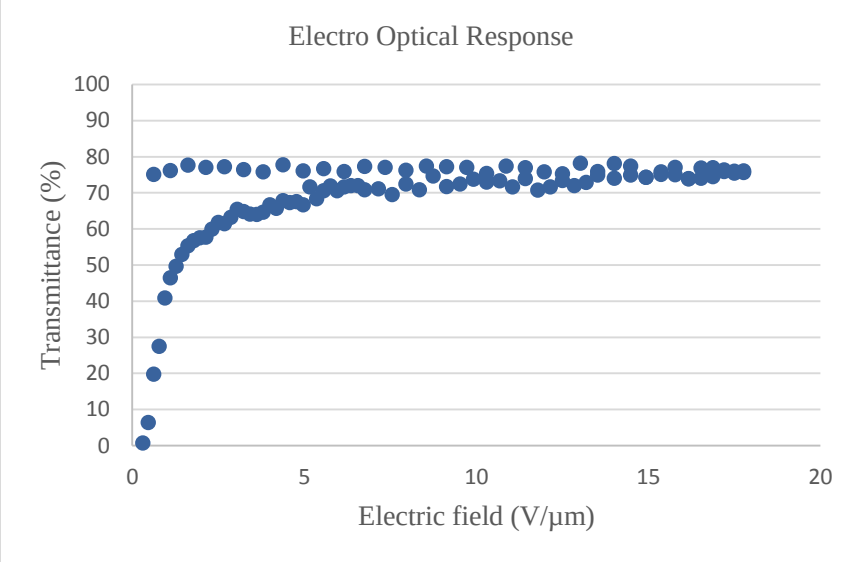


Figure III.48 - EO response for the scale-up cell

Table III.14 show the main results for the EO response to the scale-up cell.

Table III.14 - Resume for EO response for the scale-up cell

%C	%PME	Tmax %	E90 V/µm	T0	Toff
75%	96%	78%	6	0%	75%

3.5. *Erasing device by Joule heating*

The Joule heating was tested in order to erase the permanent memory.

Different values of current and voltage were applied. The voltage was adjusted until reaching the desired current and the necessary time to erase PME has been registered.

Figure III.49 show the variation of the necessary time to erase the PME with the variation of the applied current.

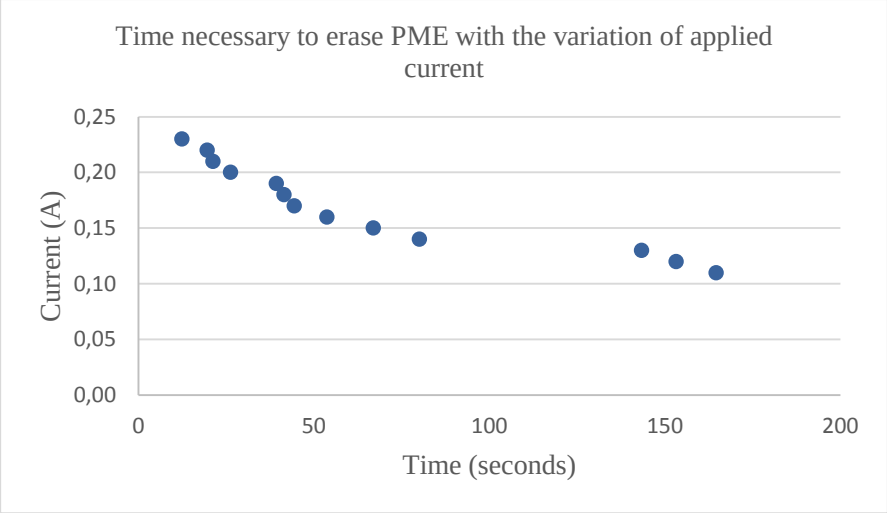


Figure III.49 - Time necessary to erase the PME with the variation of applied current

Observing the image above it is possible to conclude that decrease of the necessary time to erase the PME decreases with the increases of the applied current.

Figure III.50, Figure III.51 and Figure III.52 show the cell when the electric field is applied, when the electric field is removed and after Joule heating.

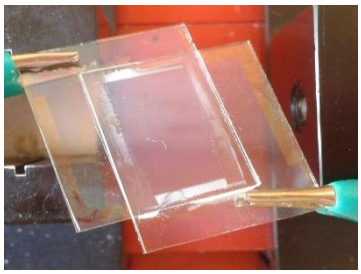


Figure III.50 – Cell when the electric field is applied

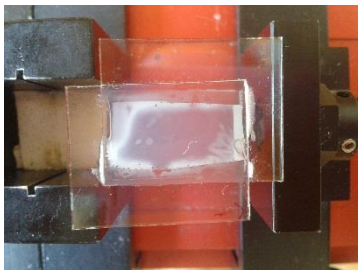


Figure III.51 – Cell when the electric field is removed

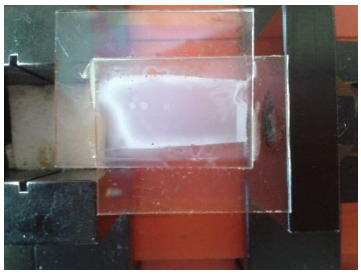


Figure III.52 – Cell after joule heating

It is possible to observe for the images above that the Joule heating erase the permanent memory effect.

IV. Chapter Four

4. Conclusions

In the present work PDLCs using E7 liquid crystal and one of two monomers, PE4A or TMT, were prepared, as well using co-polymerization between the monomer PE4A and the oligomer AP.

By the analyses performed it is possible to conclude that PDLCs produced by thermal co-polymerization with PE4A/AP proportion of 50/50 (with 1% of AIBN) and 60% of E7 liquid crystal is the more efficient PDLC concerning permanent memory effect. The PDLC showed 100% of permanent memory effect. It is believed, that this proportion of monomers/oligomers allowed an adequate adjust for the liquid crystal domains in the polymeric network, leading to weak anchorage force between the two that permits this high permanent memory effect.

As the monomers used formed a highly crosslinked polymeric network, the polymerization time it is an important variable in the polymerization reaction for the PDLCs studied.
A higher polymerization time can originated a polymeric network to much crosslinked and it is impossible to incorporate the liquid crystal micro domains in the polymeric matrix.

A 96% permanent memory effect was achieved in LC2-20 Instec commercial cells and in self-made cells, both using polyimide as alignment layer.

It is possible to erase the permanent memory effect in the PDLCs in a device applying Joule Heating. With the increase of the applied electric current to the PDLC the time to erase permanent memory effect decrease, as expected.

The time necessary to erase the permanent memory effect was between 12 seconds to 165 seconds for electric current between 230 mA to 110 mA respectively.

V. Chapter Five

5. References

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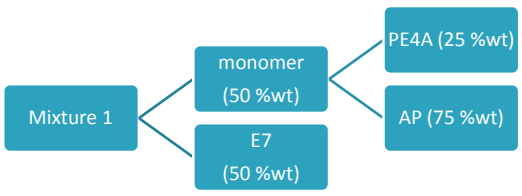
VI. Chapter Six

6. Appendix

6.1. EO analysis for building 3D graph

Each mixture has in the monomer weight 1% of AIBN.



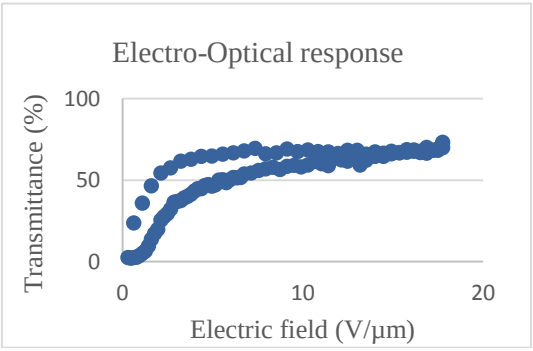
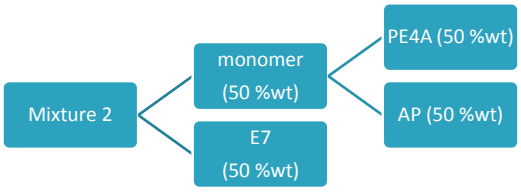


Figure VI.1 - Electro-optical response for the mixture 1



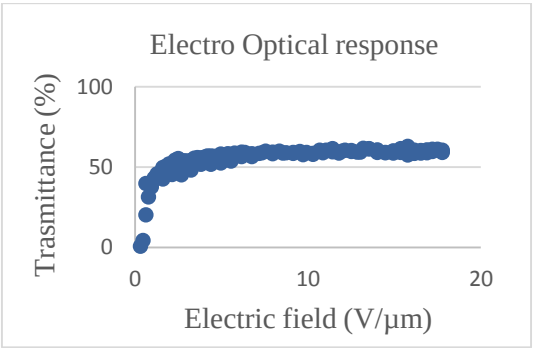
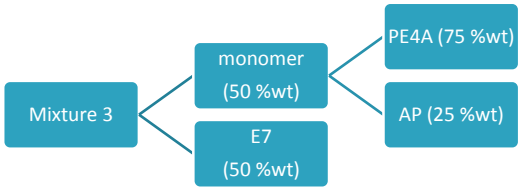


Figure VI.2 - Electro-optical response for mixture 2



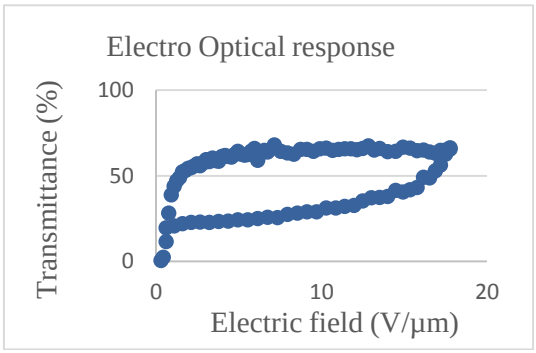
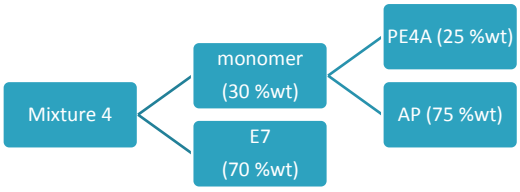


Figure VI.3 - Electro -optical response for mixture 3



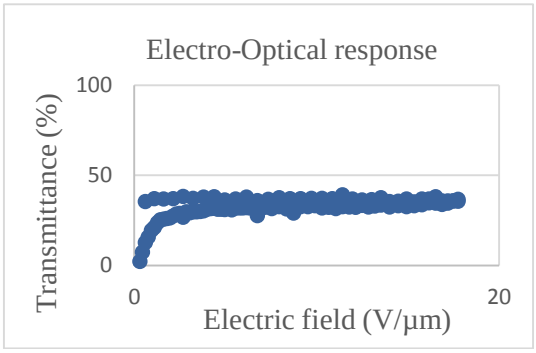
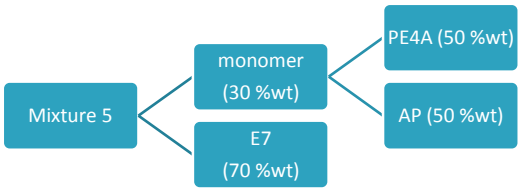


Figure VI.4 - Electro-optical response for mixture 4



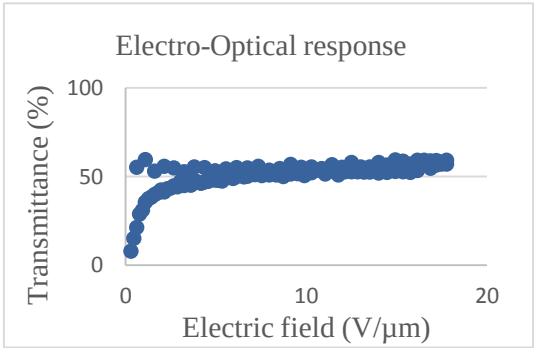
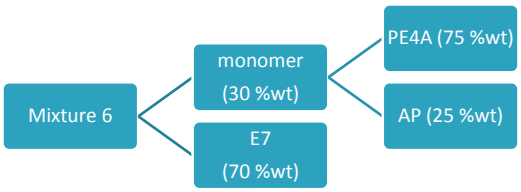


Figure VI.5 - Electro-optical response for mixture 5



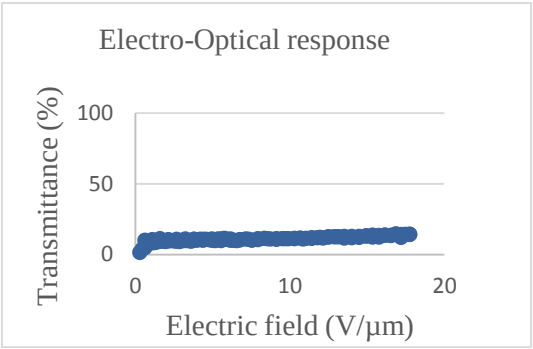
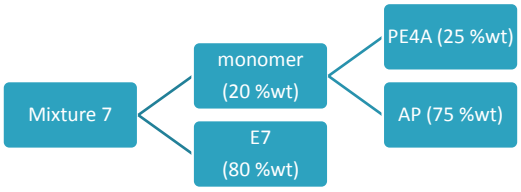


Figure VI.6 - Electro-optical response for mixture 6



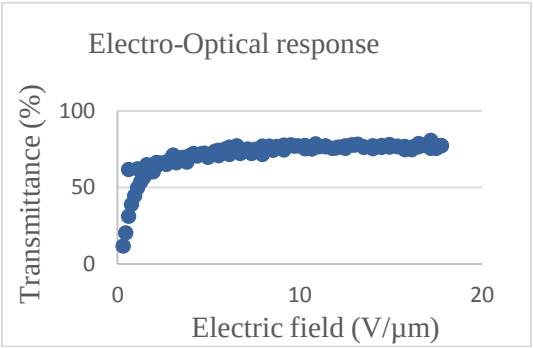
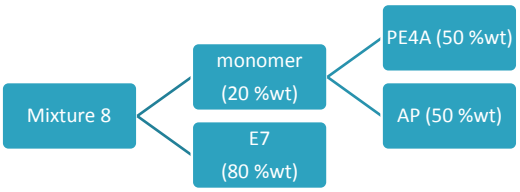


Figure VI.7 - Electro-optical response for mixture 7



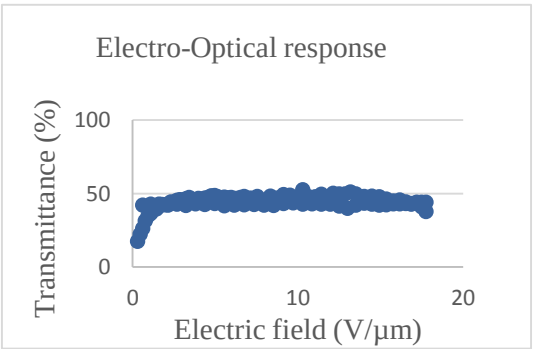
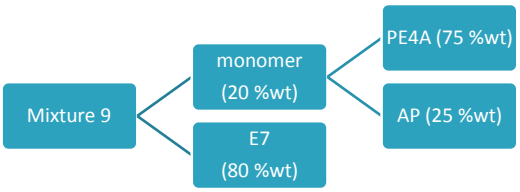


Figure VI.8 - Electro-optical response for mixture 8



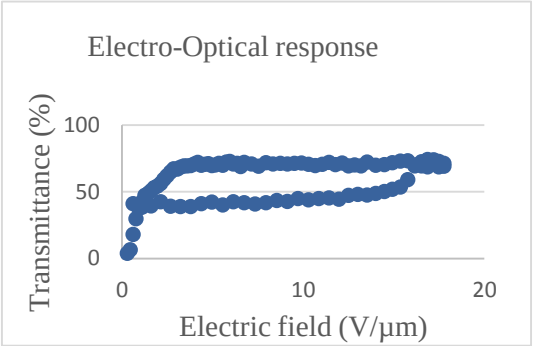
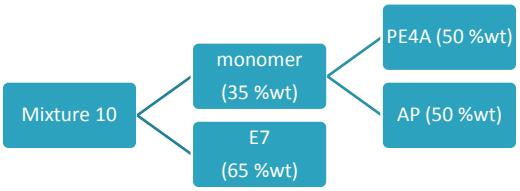


Figure VI.9 - Electro-optical response for mixture 9



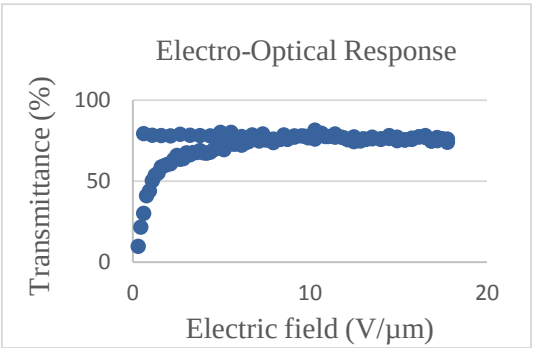
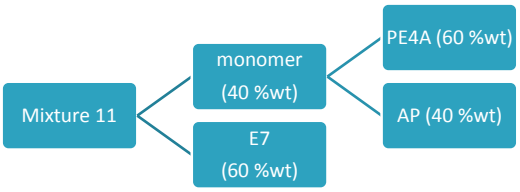


Figure VI.10 - Electro-optical response for mixture 10



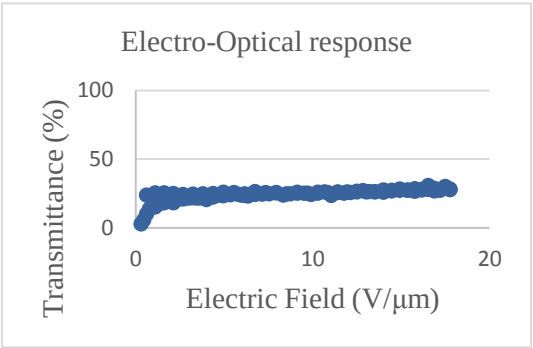
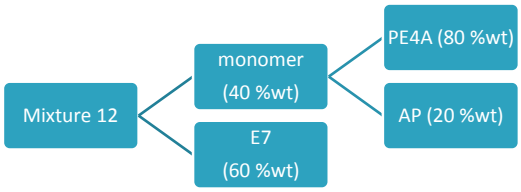


Figure VI.11 - Electro-optical response for mixture 11



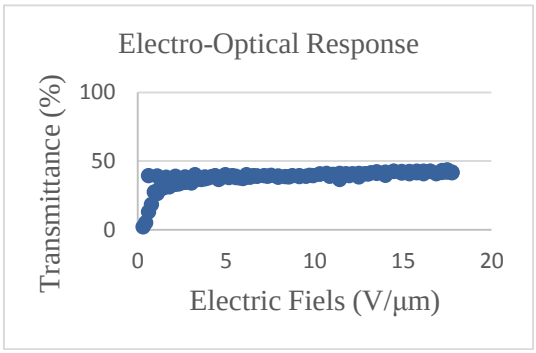
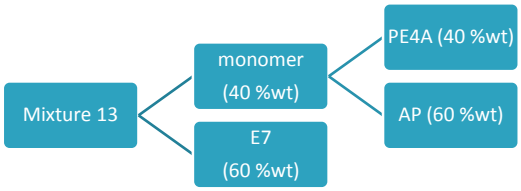


Figure VI.12 - ELectro-optical response for mixture 12



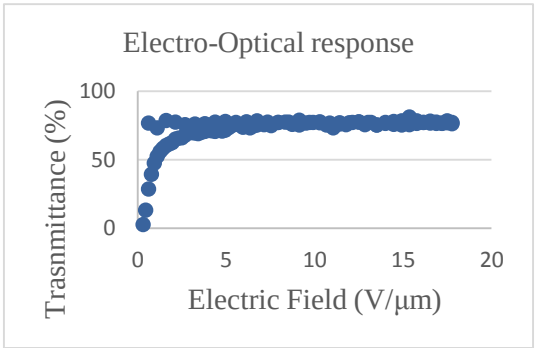


Figure VI.13 - Electro-Optical response for mixture 13

6.2. SEM analysis for two and three days of polymerization

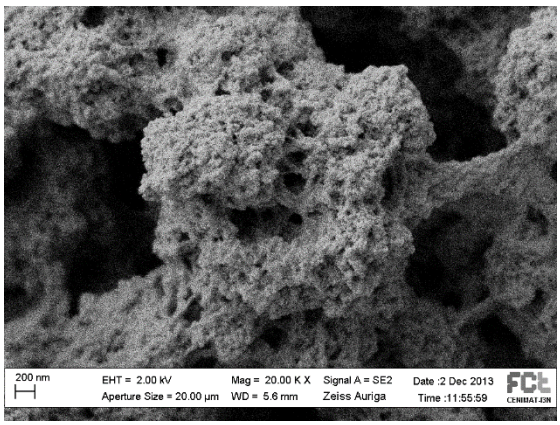


Figure VI.14 - SEM analysis for the PE4A/AP proportion of (50/50) (Magnification of 20.000 and 3 days of polymerization)

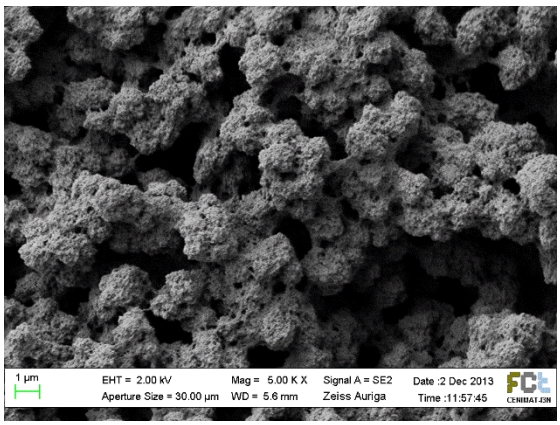


Figure VI.15 - SEM analysis for the PE4A/AP proportion of (50/50) (Magnification of 5.000 and 3 days of polymerization)

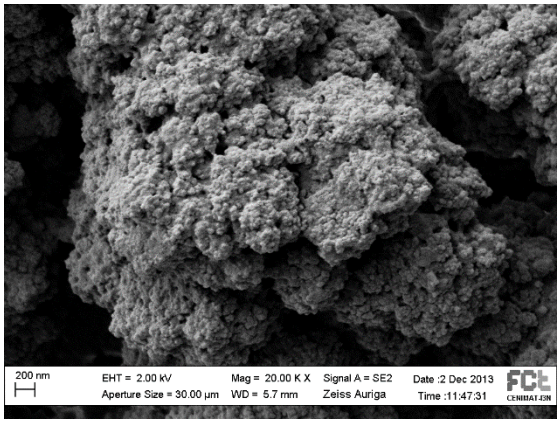


Figure VI.16 - SEM analysis for the PE4A/AP proportion of (75/25) (Magnification of 20.000 and 2 days of polymerization)

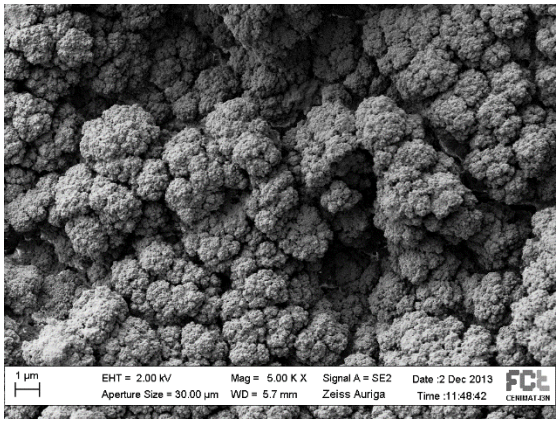


Figure VI.17 - SEM analysis for the PE4A/AP proportion of (75/25) (Magnification of 5.000 and 2 days of polymerization)

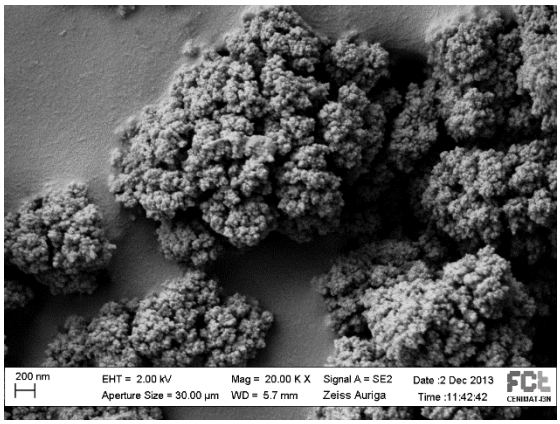


Figure VI.18 - SEM analysis for the PE4A/AP proportion of (100/0) (Magnification of 20.000 and 2 days of polymerization)

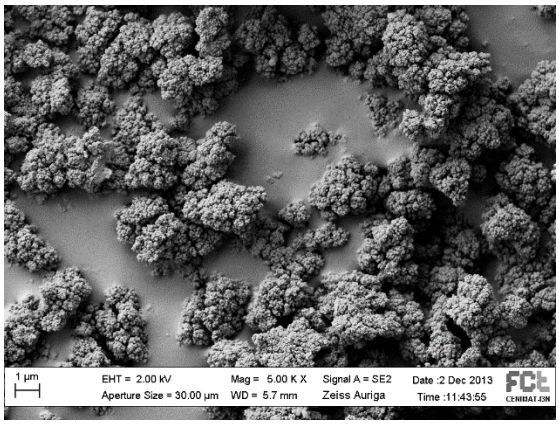


Figure VI.19 - SEM analysis for the PE4A/AP proportion of (100/0) (Magnification of 5.000 and 2 days of polymerization)

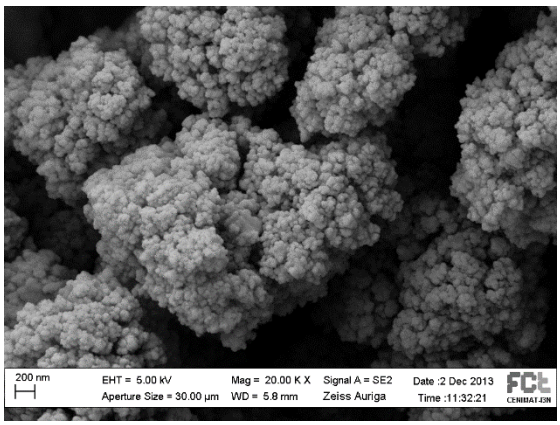


Figure VI.20 - SEM analysis for the PE4A/AP proportion of (100/0) with liquid crystal (Magnification of 20.000 and 2 days of polymerization)

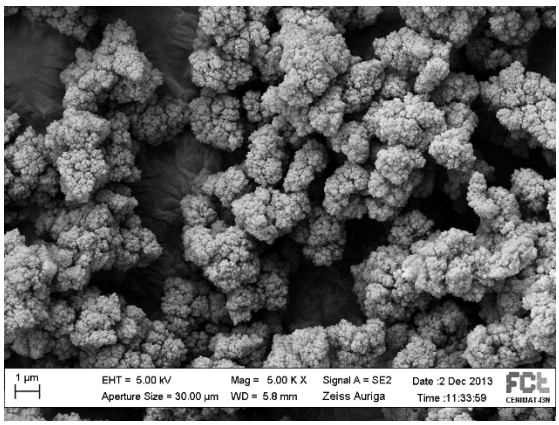


Figure VI.21 - SEM analysis for the PE4A/AP proportion of (100/0) with liquid crystal (Magnification of 5.000 and 2 days of polymerization)

6.3. DSC 3th heating cycle

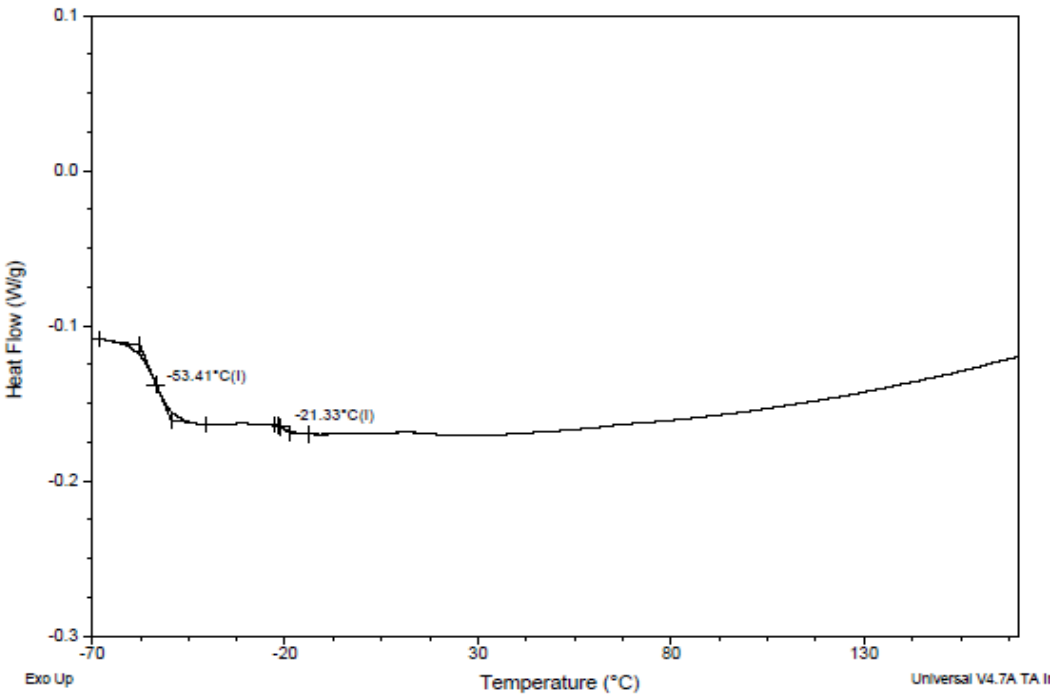


Figure VI.22 - DSC third heating cycle for AP

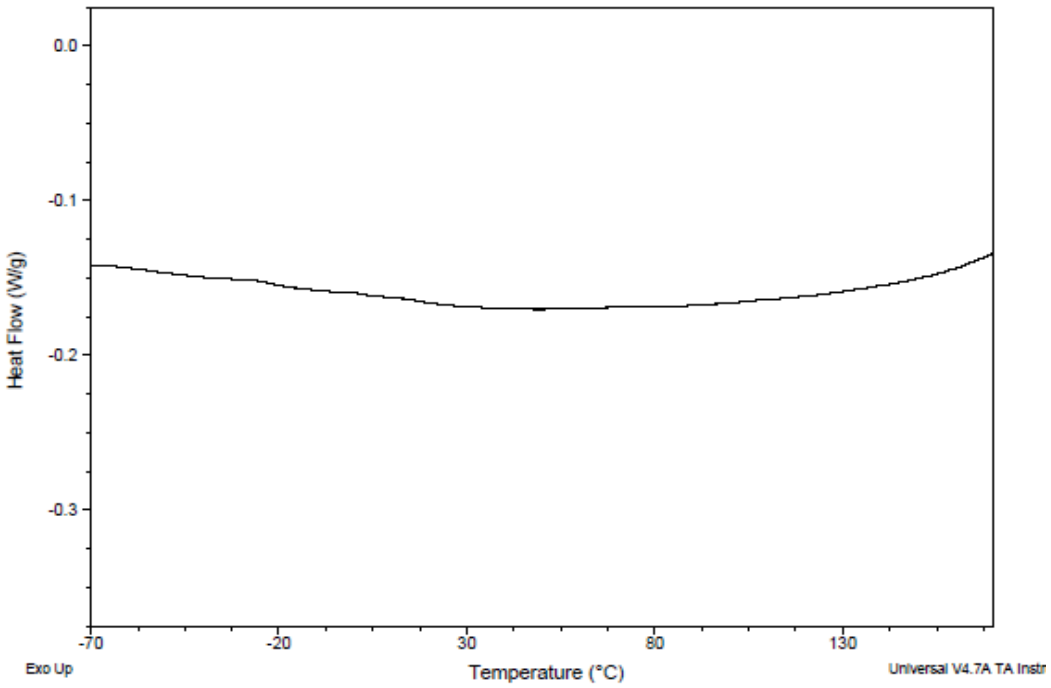


Figure VI.23 - DSC third heating cycle for PE4A

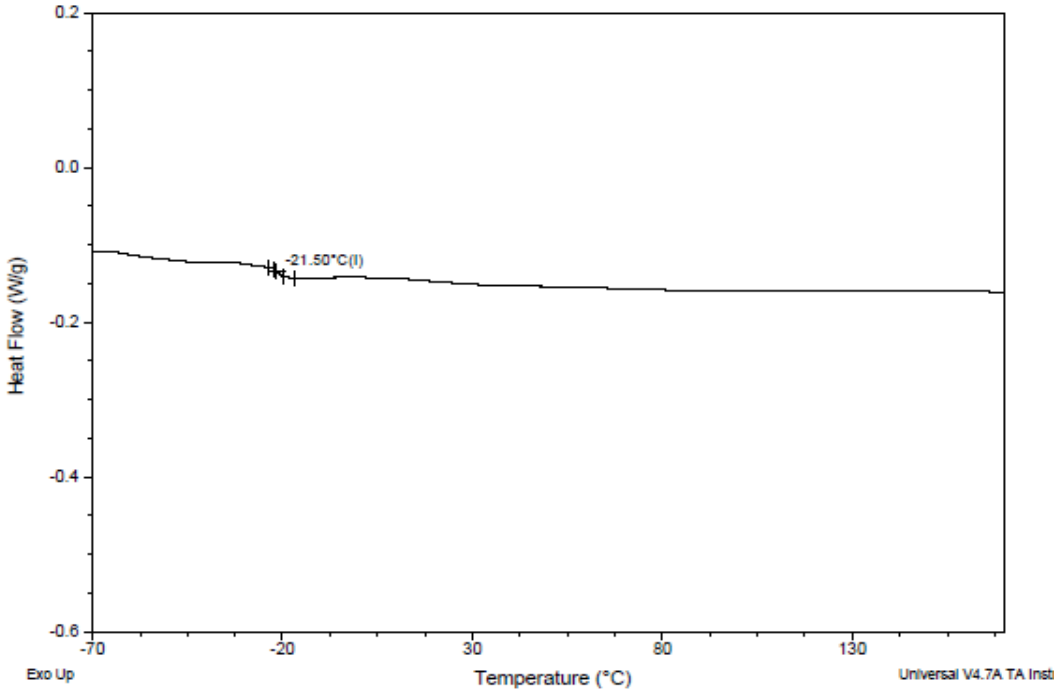


Figure VI.24 - DSC third heating cycle for PE4A/AP in the proportion of 50/50